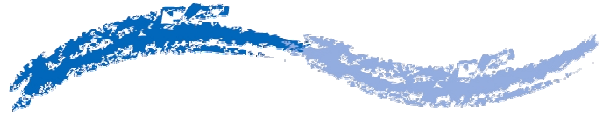


Application

for Basic Approval

To the
International Maritime Organization

Aquaworx



AquaTriCombTM
Ballast Water Treatment System

2008-10-07

Aquaworx ATC GmbH
Pettenkoferstrasse 22
D - 80336 München

QUALITY MANAGEMENT STATEMENT

This document has been prepared by AQUAWORX ATC GmbH, Germany.

The responsible author of this document is Dr. Birte Clason.

Contributions to this document have been received from

- Laboratory IBEN GmbH, Germany
- Technical University Hamburg-Harburg (TUHH), Germany
- KBL-Shipping GmbH, Germany

Document approved by:

Peter Falk, Managing Director

Document released by:

Dr. Birte Clason

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List of Abbreviations and Acronyms

AOX	adsorbable organic halogen compounds
bw	body weight
BWTS	Ballast Water Treatment System
BOD ₅	5 day biochemical oxygen demand
CAS Nr.	Chemical Abstracts Service Number
CB	cavitation bubble
d	days
DNA	Deoxyribonucleic acid
DOM	Dissolved Organic Matter
DOC	Dissolved Organic Carbon
EC ₅₀	Effect Dosis of 50 % of the population
EOX	extractable organic halogen compounds
eV	electron volt
GC-ECD	Gas Chromatographie / Electron Capture Detector
GC/MS	Gas Chromatographie / Mass Spectroscopy
HAA	Halogenated acetic acid
Hb	Hemoglobin
Hz	Herz
H ₂ O ₂	Hydrogenperoxide
ISC	Inter system crossing
ISM	International Safety Management Code
K	Kelvin
ke	elimination rate constant
kW	Kilowatt
LC ₅₀	Lethal Dosis of 50 % of the population
LFUS	Low Frequency Ultrasound
LHKW	Lightly volatile halogenated hydrocarbons
log K _{ow}	log octanol/water partition coefficient
LOAEL	Lowest observed adverse effect level
LOEC	Lowest observed effect level
LoQ	Level of Quantification
LPUV	Low Pressure UV
LWC	low weight carbonyl compounds
M	Mol
metHb	Methemoglobin
MOS	Margin of Safety
MOE	Margin of Exposure
MPUV	Medium Pressure UV
MSDS	Material Safety Data Sheets
MSF	MicroSintFilter
MTBE	Methyl Tertiary Butyl Ether
N	Newton
nm	nanometer
ns	nanoseconds
NOEC (NOEL)	No observed effect concentration
NOAEL	No observed adverse effect concentration
NSMT	Normenstelle für Schiffs- und Meerestechnik des DIN
OH•	Hydroxyl Radical
O ₃	Ozon

Pa	Pascal
PBT	Persistence, Bioaccumulation, Toxicity
pKa	acid dissociation constant
PEC	Predicted environmental concentration
PNEC	predicted no effect concentration
ppm	parts per million (mg/l)
RNA	Ribonucleic acid
RX	organic halides
SIM	Selective Ion Monitoring
SMS	Safety Management System according to the ISM-Code (ISM 2002)
SP	Sampling Point
THM	Trihalomethanes
TRO	Total Residual Oxidants
UVC	Ultraviolet C radiation
US	Ultrasound
UV _{254nm}	UV-light with the specific wave length 254 nm
λ	Wave length
μm	micrometer

SUMMARY

Aquaworx ATC GmbH is applying for the Basic Approval of the AquaTriComb™ ballast water treatment system (BWTS) at the International Maritime Organization.

The application of Aquaworx ATC GmbH for the Basic Approval of its ballast water treatment system AquaTriComb™ is based on the technologically safe and environmentally sound approach to abstain from any preparations and avoidance of reactive intermediates with the potential to pose a risk to the environment and / or to human health. The AquaTriComb™ BWTS is designed to purposely avoid reactive intermediates like OH• radicals and consequently unwanted reaction products by using monochromatic UV-light and low frequency ultrasound.

Based on definitions of GESAMP revised procedure (MEPC 58/2/7) substances generated by the treatment process of the AquaTriComb™ system are classified as: non Preparations are added and non Active Substances are generated, Relevant Substance is defined as OH• radical and Other Chemicals are defined as possible by-products.

To evaluate the impact of ballast water treatment on the production of Other Substances water samples were analysed chemically before and after the treatment process. All THM, LHKW, HAA, Bromophenol, Acetonitril, AOX, EOX and TRO (at all 32 substances or substance groups) measured before and after treatment were below Level of Quantification. One exemption being a Chloroform concentration in one sample before the treatment and is considered as an outlier. AOX could be measured in six samples before and after treatment at very low concentration at the Level of Quantification. Nitrite values showed a high variability above the Level of Quantification, in samples before as well as in samples after the treatment process. To verify a significant assertion regarding the variability of the results a statistic test calculation was performed. The Mann-Whitney U test statistic was used on the basis that data were not normal distributed. Results of the test statistic showed, the data from samples before and after treatment were significantly not different, whereby they belong to the same data population. Therefore it can be concluded that Nitrite is not generated by the treatment process. All Nitrite values before and after treatment are within the German, EU, EPA and WHO drinking water regulations. Hence, and based on the measured data, no risk for human health and the environment can be diagnosed.

Under independent scientific examination the risk characterization and risk assessment was conducted regarding risks to the safety of ship, to human health and to the aquatic environment. Even if Nitrite values result from high background values originated in the test water and not from the treatment process, literature data of risk characterisation and assessment for Nitrite was conducted.

Analysis of the risk assessment demonstrate that no risks associated to the ship and its personnel neither to human health in general could be identified. Additionally it can be concluded that from this treatment process the magnitude of the hazard and the probability of risk exposure to the aquatic environment is of no concern.

Based on analytic results and risk assessment it can be concluded also that even if the precisely adjusted US and UV technology generates OH• radicals by means of photons and cavitation bubbles, the concentration of OH• radical related Other Chemicals would be insignificantly low (not present, or at non-measurable concentrations) and risks to human health and to the environment can be demonstrably excluded.

Therefore, this application for Basic Approval is connected to the appeal to whether the AquaTriComb™ BWTS proposal can be assessed according to the Guidelines 8 of the Ballast Water Convention.

1 INTRODUCTION

Aquaworx ATC GmbH is applying for the Basic Approval of the AquaTriComb™ ballast water treatment system (BWTS) at the International Maritime Organization.

The application is connected to the appeal to examine whether the AquaTriComb™ BWTS proposal can be assessed according to the Guidelines 8 of the Ballast Water Convention, following the guidance and format provided in the revised Draft Methodology (MEPC 58/2/7). This is due to the fact that no Preparations are intentionally introduced or generated with the technology.

The AquaTriComb™ BWTS is composed of pre- and after-treatment modules to disinfect aquatic species in the ballast water. The treatment system comprises mechanical filtration in combination with ultrasonic (US) oscillation for filter self-cleaning, and ultraviolet-C (UV-C) radiation also in combination with ultrasound for self-cleaning of UV-C lamps.

Due to the highly efficient combination of US oscillation and UV radiation the AquaTriComb™ technology can abstain from any Preparations or chemical additives, which may pose a hazard to the population and / or to the environment.

Because the US and UV-C technology is precisely adjusted to avoid the generation of OH• radicals, the concentration of the OH• radical related Other Chemicals is that low that risks to human health and to the environment can be demonstrably excluded.

UV-C and US are especially acknowledged in portable- and waste water management to produce no, or little disinfection by-products by themselves (Zoeteman et al 1982, Anderson et al. 1982, Suslick 1989, de Veer et al. 1994, Oppenländer 2003, Blume & Neis 2004, Endresen et al. 2004, Hijnen et al. 2006, Liu et al. 2006, Yasui et al. 2007) and have been identified as the most environmental friendly and effective methods for ballast water treatment (Oemcke 1999, Sutherland et al 2001, Dobbs & Rogerson 2005, Gavand et al. 2007, Holm et al. 2008, Umweltbundesamt 2008).

All reactive intermediates generated by UV-C radiation and ultrasound, and their potential reaction products during ballast water treatment occur naturally in seawater as products of sunlight induced photolytic activities (Palenik et al. 1991, de Mora et al. 2000). In natural seawater reactive intermediates play an important role in the degradation of dissolved organic matter (DOM; largely uncharacterized long-chain organic molecules) enhancing biodegradability by micro organisms of such substances and thus are important for the oceanic carbon cycle (Cooper et al. 1989, Hoigné et al 1989, de Mora et al 2000, Pullin et al. 2004). However, the AquaTriComb™ Ballast Water Treatment System is designed to purposely avoid reactive intermediates and consequently unwanted reaction products by using monochromatic UV-light and low frequency ultrasound (Portenlänger & Heusinger 1997, Mason and Lorimer 2002, Liu et al 2006, Holm et al. 2008).

The radical abandonment of any Preparations and avoidance of reactive intermediates qualifies the AquaTriComb™ technology as a highly effective and particularly environmentally sound ballast water treatment system.

1.1 Ultraviolet radiation

Ultraviolet technology is proving more and more successful and is being used as an acknowledged, cost-effective and reliable process. UV-C radiation as disinfection mean is well known for almost hundred years and is utilized widespread in the sector of disinfection of portable water, aquaculture waters, cooling water, hot water systems, ultra pure water, food-stuff industry, medicine, bottling of drinks, etc. It is used primarily wherever the microbiological requirements are particularly high, or where chemical disinfectants are unacceptable for

quality or environmental reasons. It was found that especially a wave length of 254 nanometer (nm) has a strong performance for disinfection. The low pressure mercury germicidal lamps, which are used for the UV-disinfection have their maximum performance at a wave length of 254 nm, and are similar to the absorption curve of the DNA.

The use of UV-radiation as disinfection energy results in no change of the chemical compositions ph-value, temperature, salinity, taste, odour and colour of the solution being treated, and safety issues related to the handling of Relevant and / or Other Chemicals are eliminated.

Ultraviolet disinfection requires a minimum dosage to be effective. The applied dosage is a function of the lamp intensity and the exposure time. These parameters are directly affected by equipment configuration, flow path of the water along the bank of lamps, the solids content, and the turbidity of the water to be disinfected. Compared to mid- or high pressure lamps, low pressure lamps can only operate with a lower performance, but they have a much better efficiency of about 45 %. Using high- or mid pressure UV lamps, the operating costs will be higher. Due to this facts, for the disinfection application of the treatment of ballast water low pressure lamps are installed in the AquaTriComb™ BWTS.

The low pressure mercury vapour lamps consist of one hermetically closed discharge vessel. The gas inside is a vacuum seal against the outside. A voltage will be generated, which generates an electrical field between the electrodes. If the accelerated voltage is high enough, electrons will leave the electrodes and will be accelerated in the electrical field. If they crash with the gas atoms they discharge their kinetic energy. The atom or molecule decreases to a lower energetic level, or to the basis level. This released energy will normally be emitted in kind of radiations, so called "quants". Due to the energy in the atom, mercury is a very suitable gas for production of UV-radiation.

It is a scientifically well known fact, that resistance of organisms like bacteria, viruses, moulds or fungal spores to ultraviolet radiation cannot be acquired. Most pathogenic germs are especially sensitive to UV-radiation. An important advantage of physical disinfection is that the sensitivity to UV still functions even when germs have already built up resistance to conventional disinfection measures such as alcohol, antibiotics, chlorinated chemicals etc. A lot of conventional medical equipment and systems are now reaching the limits of their capabilities for disinfection and prevention when dealing with this problem.

To address all the mentioned needs, UV-radiation as part of the AquaTriComb™ technology provides a powerful barrier to chemical contaminants while simultaneously disinfecting to avoid the dispersal of invasive aquatic species by ballast water from ships.

The prime affect on organisms through short wave and energetic UV-C radiation at 254 nm is based on a photo-chemical alteration of the DNA. The UV-C radiation is absorbed by pyrimidins, which form the basic elements of the organic base of the DNA string. Through covalent bindings of two neighbouring bases like thymine, pyrimidine dimers are generated. These pyrimidine dimers avert replication of DNA helix strings and cause mutations which result from unsuccessful DNA string repair mechanisms. Dimers are called "bulky lesions": they disturb the helical configuration of DNA by means of partial decartelization resulting in reduced base matching ability. In addition the UV radiation may result in direct alterations of the DNA morphology, for example singular or double string fractures. Double string fracture can not be repaired and lead to cell mortality. In general UV radiation result in defects of DNA repair abilities (Eckhardt-Schupp 2006).

The advantages of the application of UV-radiation as disinfection process are:

- A purely physical disinfection process;

- No Preparations will be added nor intentionally produced;
- Tried, tested and proven process approved by the DVGW (DVGW 2001);
- Water disinfected by UV-C radiation conforms with German portable water regulations (TVO, BGI 2001);
- No formation of health damaging by-products;
- No production or storage of chemicals onboard necessary, and no danger of over- or under dosing;
- Only naturally occurring processes are used;
- No change in physical parameters like pH-value, temperature, salinity, taste, odour, colour;
- The use of UV-C radiation does not increase corrosion in ship compartments;
- Low maintenance and operating costs of the UV reactor compartments;
- Low energy consumption needed by UV-C technology.

UV-C radiation as disinfection technology of ballast water generates no harmful environmental effects to the aquatic environment.

1.2 Ultrasonic oscillation

The special advantage of ultrasonic (US) oscillation is the very fast and extremely high cleanness of the parts without any manual works to be carried out, and without any damage to the components. Also persistent impurities in, for example borings and / or hollow spaces or at technically complicated parts will be removed by ultrasonic oscillation in seconds.

Ultrasonic applications can be found, for example, in the aviation industry, laboratory medicine, textile and plastic industry, print and semi-conductor industry, surface engineering etc. US cleaning and scouring is carried out with engine blocks, ball bearings, valves, filters, nozzles, breathing apparatus, mechanical measurement and calibration device, analytic strainer etc.

The germicidal effect of high frequency ultrasonic waves is assigned to cavitation and its direct after-effects like shearing, pressure, local calefaction and generation of free radicals by sonoluminescence (electric discharge) during treatment in fluid media. It results in affection of the cell wall, the cell membrane and other functional cell elements (Save et al. 1994).

The advantages of the use of ultrasound are:

- US processes are purely physical processes;
- The use of cavitation does not increase corrosion in ship compartments;
- Brushing or other means of cleaning is dispensable;
- Fast, highly efficient cleaning;
- Maintenance free, no personnel training needed;
- Extremely low energy consumption.

1.3 Technology Overview

Aquaworx ATC GmbH has developed a ballast water treatment system comprising pre- and after treatment modules. For the BWTS test plant the volume flow rate is designed at 250 m³/h. The capacity of the volume flow rate can be designed by means of aligned up-scaling of the modules.

During ballast water intake and at pre-treatment stage the ballast water is filtered through three (3) identically constructed MicroSintFilter (MSF) modules to remove particles and organisms. Pre filtration allows very effective removal of organisms (Cangelosi et al. 2007).

Instead of so far applied 50 μm , the Aquaworx filter pore size equals 35 μm ; filter material consists of a sintered high grade steel alloy (Monel 400 material, W. No.: 2.4360, UNS: N04400)¹. The automatically self-cleaning process of the filter modules is realized via permanent ultrasonic oscillation inside the filter tube. The ultrasound dissolves organic (bio film, agglutinations) and inorganic (e.g. calcium carbonate) accumulations from the filter tube, and organic agglomerations (detritus particles, phytoplankton colonies, slime creating phytoplankton) in the ballast water are broken off, and organisms are pre-treated. By means of reversed flow rate the backflush water is disposed off via separate piping.

After-treatment is processed inside the UV-reactor via UV-C low pressure mercury germicidal lamps and low frequency ultrasound. The application of low pressure UV-technology at 254 nm wave length disinfects aquatic organisms very effectively.

The most important impact of the ultrasound is the highly effective and permanent cleaning of the UV-emitter through the ultrasonic transmission along the full length of the UV-reactor, avoiding accumulations of bio films or inorganic salts on the quartz-crystal tubes. In addition, organic particles and phytoplankton colonies are broken off and organisms are pre-treated. Additionally, inside the UV-reactor the organisms are lethally affected by UV-light and ultrasound.

During de-ballast operations the ballast water from the tanks is pipelined through the complete pre- and after treatment plant before discharge. Organisms, e.g. bacteria and monocellular phytoplankton, which in spite of effective treatment may grow again during long ship voyages, will be effectively killed. For de-ballast water treatment the "Reactor In Reactor" (RIR) has been developed.

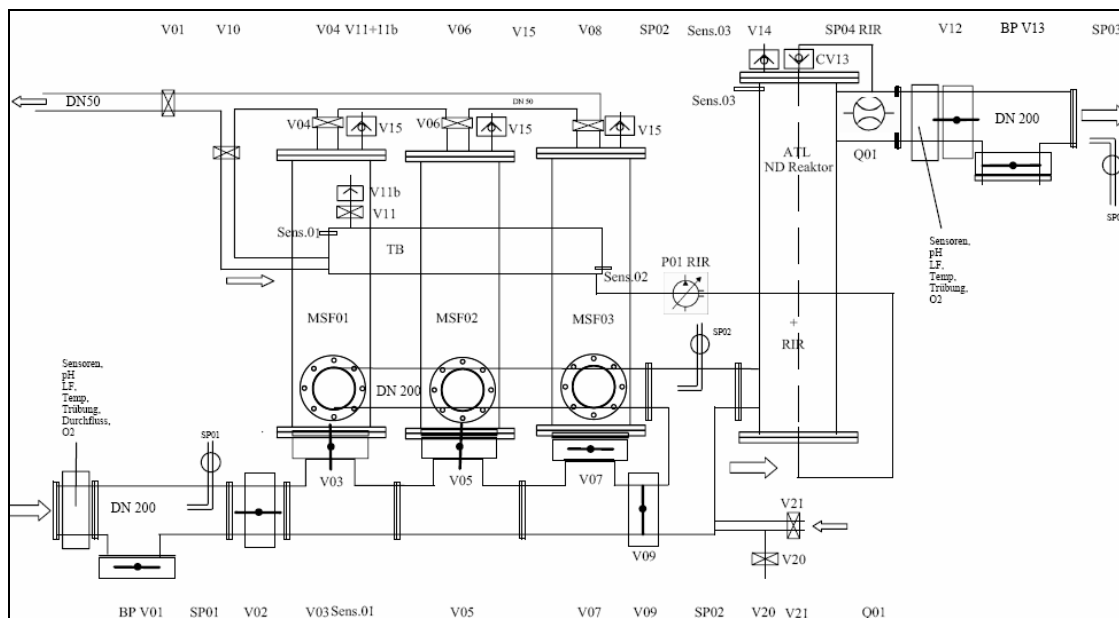


Figure 1: Aquaworx ballast water plant consisting of three identically constructed MSF-modules (MicroSintFilter), Transfer container (TB) and UV reactor AquaTriLight including RIR (Reactor In Reactor).

¹ Specification Monel 400: melting point:1350 °C, tensile strength 400 – 600 N/mm², feather-hard 850 – 1050 N/mm², sheer modulus 65,3 kN/mm², application temp.: -196 to + 230 °C

During filtration of ballast water the backflush valves are closed (dead end filtration). After an intermediate storage in the transfer container, the backflush is pipelined through the UV reactor via separate tubes very close along the UV tubes (20 mm distance) which results in an extremely effective treatment through the high energetic impact of the UV radiation at a relatively low volume flow rate of approximately 10 l/min.

As illustrated in Figure 1 the biological samples are taken in between the ballast water pump and the treatment plant (SP 01), in between the pre- and after treatment (SP 02), and behind the after treatment (SP 04). At the sampling port SP 03 the quality of the backwash after disinfection can be measured during de-ballast operations.

The a-biotic parameter as pH, conductivity, temperature, turbidity, oxygen content, flow rate volume and pressure are recorded during tests online via automatic sensors. The sensors are located at the ballast water feed pipe and behind the after treatment.

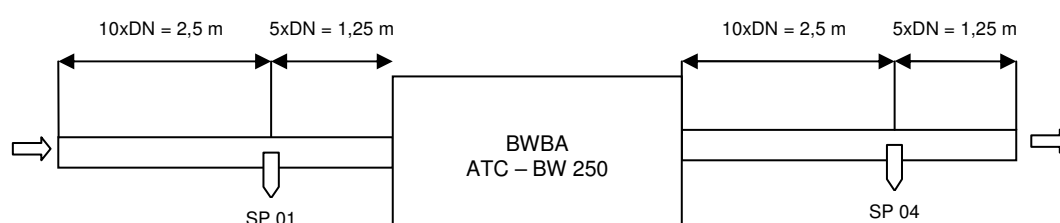


Figure 2: Location of sampling ports SP 01 and SP 04 acc. to NSMT draft

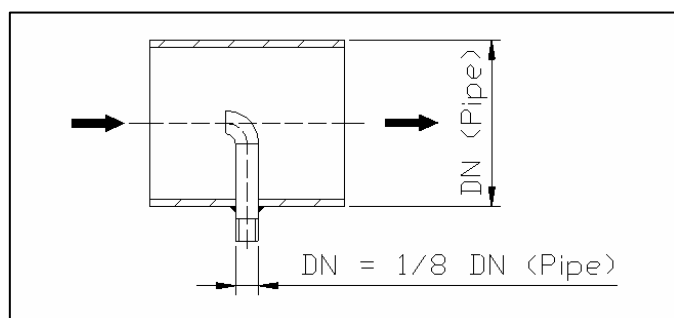


Figure 3: Design of sample piping acc. to NSMT draft

The piping diameter of the sampling points will be 1/8 of the ballast water pipe diameter, i.e. $250/8 = 31,25$ mm (Figure 3).

All valves are fitted with flanges, and electrical-driven and manual actuators. In addition to the valve positions "Open" and "Close" intermediate positions are possible.

In case of repair and maintenance or malfunction the complete treatment plant can be bypassed with by-pass valves V01 and V03, and shut-off safety valves V02 and V012.

1.4 Conclusion: technology overview

The advantages of the AquaTriComb™ ballast water treatment plant ATC-250 may be summarized as follows:

- Radical abandonment of any Preparations and avoidance of reactive intermediates
- Pore size of sinter filter (MSF modules) equals 35 µm

- During de-ballast operations the UV reactor completely disinfects the discharge water by means of pre-treatment (filter and ultrasound) and after-treatment (ultraviolet radiation and ultrasound).
- The application of ultrasound provides a high clearance performance of the sinter tubes (filter) as well as the UV-tubes.
- High disinfection performance through combination of low pressure UV-C radiation and ultrasound.
- Innovative technological optimization of filtration, ultrasound and UVC with extremely effective separation of particles and sediments, and mortifying of organisms allows for low energy consumption of approx. 13 kW only.
- As ultrasound effects are limited to the treatment plant components, cavitation effects on the ships' piping and tank system are not possible, whereas the treatment plant components are designed to cope with cavitation.
- The application of low pressure radiation and very low frequency ultrasound (20 Hz) with extremely short termed ultrasound impact (< 1 s) generated, based on analysis of treated water, none Other Chemicals during the treatment process
- By the application of UV-disinfection micro-organisms can not develop resistance; therefore also resistant pathogens (e.g. chlorine resistant) are inactivated by UV-C radiation.
- UV-C radiation and ultrasound do not effect physical parameters like salinity or pH-values of the ballast water.

2 IDENTIFICATION OF PREPARATIONS, ACTIVE SUBSTANCES, RELEVANT AND OTHER CHEMICALS (G9: 4.1)

2.1 Chemical Identification

Based on the definitions of “Preparations”, “Active Substances”, “Relevant Chemicals” and “Other Chemicals” as outlined in the revised Methodology for information gathering and the conduct of work of GESAMP-BWWG (MEPC 58/2/7) substances used or generated by the AquaTriComb™ BWTS are classified as follows:

2.1.1 Preparation

means any commercial formulation containing one or more Active Substances including any additives:

The AquaTriComb™ BWTS does not utilize any “Preparation” besides UV-light and low frequency ultrasound.

Not applicable.

2.1.2 Active Substance

means a substance or organism, including a virus or a fungus that has a general or specific action on or against harmful aquatic micro-organisms and pathogens.

The AquaTriComb™ BWTS would produce “Photons” emitted by the low pressure UV (LPUV) system, and “Cavitation Bubbles” generated by the low frequency ultrasound (LFUS) system. The photon and cavitation bubble are entirely responsible for the inactivation of harmful aquatic micro-organisms and pathogens present in ballast water (de Mora et al. 2000; Blume & Neis 2004, Hijnen et al. 2006, Holm et al. 2008).

With regard to the Methodology both can not be classified as a substance or organism, therefore they are defined as reactive physical processes, not as Active Substances. For this reason non Active Substances are generated by the treatment process.

2.1.3 Relevant Chemical

means transformation or reaction products that are produced during and after employment of the ballast water management system in the ballast water or in the receiving environment and may be of concern to the ship’s safety, aquatic environment and/or human health.

The AquaTriComb™ BWTS regards only the hydroxyl radical (OH•) as a “Relevant Chemical”. However, the amount of OH• potentially produced in the system is extremely small (Zepp 1987, Mopper & Zhou 1990, Zhou & Mopper 1990, Hua & Hoffmann 1997, Petrière & Francony 1997, Portenlänger & Heusinger 1997, Brezonik & Fulkerson-Brekken 1998, Vaughan and Blough 1998, de Mora et al 2000, Takeda et al. 2004, Abu-Hassan et al. 2006, Yasui et al. 2007). The OH• radical reacts at nearly diffusion controlled rates with any organic compound and exists for about 10⁻⁹ seconds.

Therefore OH• is considered not resident in the treated ballast water and causes no harm to the environment upon discharge.

2.1.4 Other chemicals

means reaction by-products that could be formed in the ballast water upon treatment with AquaTriComb™ BWTS.

During the process of OH-generation through photolytic and sonolytic processes secondary reactive intermediates and stable products can be formed. Most of the known stable products are non-toxic hydrocarbons. However, the formation of potential eco-toxicological Other

Chemicals is partly known or can be inferred from application of UV and US in portable and waste water treatment. Chemicals are specified under chapter 2.7.

2.2 Background to characterize Reactive physical processes, Relevant and Other Chemicals

2.2.1 Reactive physical processes (G9, 2.1.1)

2.2.1.1 The photon

According to the wave / particle-duality light can be considered as energy propagating as a wave and as a stream of photons with the constant speed of light. A photon is defined as a quantum of electromagnetic energy at a given frequency. Consequently, a photon possesses the more energy the shorter the wave length (Tipler 1995). The energy characteristic for a photon at a specific wave length is determined as:

$$E = hc/\lambda \quad (1)$$

Where E is energy in Joule, h is the Planck constant, c is the speed of light and λ is the wave length in meters.

Ultraviolet light (UV) is part of natural sun light. Electromagnetic wave length spectrum of UV (UV spectrum) is 100 – 400 nm bordered by x-ray radiation (< 100 nm) and visible light (400 - 700 nm). According to the draft of ISO-standard on determining solar irradiances (ISO-DIS-21348) the UV spectrum is subdivided into UV-A (long wave, 315 – 400 nm), UV-B (medium wave, 280 – 315 nm), UV-C (100 – 280 nm), and vacuum UV (10 – 200 nm).

UV-C can be used as a disinfectant against micro-organisms and pathogens including bacteria, viruses and phages (Hijnen et al. 2006). Therefore, UV-C is also referred to as germicidal light. Germicidal light is successfully applied in portable and waste water management (Masschelein 2002, Oppenländer 2003) and the disinfection of water in aquaculture (Liltved et al. 1995, Liltved & Cripps 1999, Munro et al. 1999). The applicability of UV in the treatment of ballast water of ships has been tested successfully in the laboratory and on the large scale (Omecke 1999, Southerland et al 2001, Laroussi 2002, Waite et al. 2003, Welschmeyer et al. 2004).

The basic process of disinfection with UV light is photolysis. Photolysis is the decomposition of a molecule by light. The strength of the chemical bond determines the photonic energy necessary for cleavage. Photonic energy of UV-C ranges from 4,43 to 12,40 eV. A photon of UV_{254nm} contains 4.89 eV photonic energy.

For water disinfection two different UV techniques are widely used differing in their UV emission spectra. Middle Pressure UV (MPUV) lamps emit light over a broad range of UV and visible light. Low Pressure UV (LPUV) lamps used in the AquaTriComb™ BWTS emit monochromatic light at the specific wave length of 254 nm (UV_{254nm}) to specifically take advantage of the DNA damaging effect, and reduce the formation of potential by-products. The use of UV_{254nm} by the AquaTriComb™ BWTS LPUV-system is discussed under chapter 2.2.2.1.

Absorption time for a photon by a molecule is in the range of nano- to picoseconds. It is generally accepted that photons leave no residuals in water. Accordingly the use of UV for water disinfection and treatment (including ballast water treatment) is considered a purely physical process producing negligible amounts of by-products (DVGW 2001, USEPA 2006, Umweltbundesamt 2008).

2.2.1.2 The cavitation bubble

Sound is a form of energy. Sound is generated by the vibration of molecules in media (air, water, solid matter) and is travelling as a wave. The wave length is defined as:

$$\lambda = c/f \quad (2)$$

where c is the speed of sound and f is the frequency. Acoustic sound frequency range is 20 Hz to 20 kHz. Above a frequency of 20 kHz up to 500 MHz (for liquids and solids) sound becomes inaudible and is referred to as ultrasound (US) (Tipler 1995).

The uses of US within this large range of frequencies are usually divided into two areas. i.e. low frequency US (20 to 100 kHz) and high frequency US (up to 10 MHz) (Mason & Lorimer 2002). Ultrasound has a broad range of application in industry, medicine and water treatment. In water treatment mechanical and sonochemical properties of US are used to remove (micro-) organisms, chemical pollutants, to break down aggregations of particles and to clean filtration units. Ultrasound applied to water has not enough energy to cause chemical reactions or mechanical disruption itself (Mason & Lorimer 2002).

Chemical and mechanical properties rely on cavitation bubbles formed by US in liquids. Wave-like motion of US through water is characterized as an oscillation of compression and rarefaction. If the negative pressure during rarefaction is high enough the molecule structure of water is destroyed and gas filled cavitation bubbles (CBs) are generated. Cavitation bubbles collapse violently releasing a shock wave and create shear stress causing mechanical disruption of material or organisms in close vicinity. According to this “hot-spot-theory” drastic localized conditions are produced: temperatures of 2000 to 5000 °K and pressures of 1800 to 3000 atm occur in the CB (Mason & Peters, 2002).

As so, the CB itself acts as a micro-reactor triggering chemical reactions inside and outside the bubble. Hydrogen radicals ($H\cdot$) and hydroxyl radicals ($OH\cdot$) can be generated inside the CB (Riesz et al. 1985). Chemical reactions on the outside depend on the release of reactants formed inside the CB.

In and around the micro-reactors four possible reaction sites for the generation and/ or reaction of radicals associated with the collapse of the cavitation bubble are stated, which are

- i) the gas filled cavity interior. During the sonolysis of the solvent or volatile compounds radicals or other activated molecules can be generated in there.
- ii) the liquid shell around the bubble in which reactions happen caused by the radicals expelled from the bubble interior
- iii) the liquid medium around the bubble in which consecutive radical reactions can follow and
- iv) the lipid droplets inside the bubble where also reactions of the radicals produced in the hot gas phase take place (Mason & Peters 2002).

The contribution to the formation of radicals (mainly $OH\cdot$) by using low frequency ultrasound will be discussed in chapter 2.2.2.2.

Size and energy release of the CB upon collapse are frequency dependent. At low frequencies CBs are bigger and collapse more violently compared to higher frequencies. At low frequencies the temperature generated during collapse of the CB is high enough to consume most of the reaction products (e.g. radicals) inside the bubble and the release of reactants is negligible. At high frequencies the bubble’s lifetime is shorter and collapse occurs very quickly, thus enhancing the possibility of radical ejection before radical recombination inside the bubble (Petrier & Francony 1997, Petrier et al. 1994). Once ejected the generated radi-

cals may react with compounds present in the media. Accordingly, mechanical properties of US like disinfection dominate at low frequencies, while sonochemical processes e.g. mineralization of non-biodegradable compounds dominate at higher frequencies.

The life time of a CB created at low frequency 20 kHz in water is in the range of μ s to ms, where life-time is mainly limited by collision (Luther et al. 2001). The CB itself is not resident in the water and consequently causes no harm upon release of treated ballast water.

2.2.2 Relevant chemical ($\text{OH}\cdot$) (G9, 2.1.4)

We consider the hydroxyl radical ($\text{OH}\cdot$) as the only Relevant Chemical formed during the process of BWT by the AquaTriComb™ BWTS. Since $\text{OH}\cdot$ is highly reactive a number of chemicals could be produced in the treated ballast water theoretically. The eco-toxicological most Other Chemicals are specified under chapter 2.7.

Formation of $\text{OH}\cdot$ can in general be initiated by both, UV-irradiation and US. In the following, we are going to show by literature review and the results of chemical testing of ballast water treated by the AquaTriComb™ BWTS, that:

1. The AquaTriComb™ BWTS is specifically designed to avoid the formation of $\text{OH}\cdot$
2. Therefore, amounts of $\text{OH}\cdot$ produced are extremely small (at all, and in comparison to other techniques)
3. Consequently, potential formation of eco-toxicological relevant by-products is extremely low and concentrations are negligible and were not detectable in ballast water treated by the AquaTriComb™ BWTS

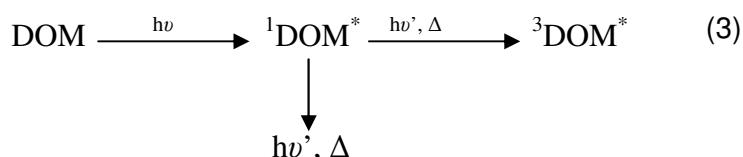
2.2.2.1 Formation of $\text{OH}\cdot$ by $\text{UV}_{254\text{ nm}}$

Formation of $\text{OH}\cdot$ and other reactive intermediates is a natural process in sunlit natural seawater. Sources for $\text{OH}\cdot$ in seawater next to DOM are Nitrate (NO_3^-), Nitrite (NO_2^-) and H_2O_2 . While NO_3^- and NO_2^- are largely of anthropogenic origin in coastal regions (eutrophication), H_2O_2 is formed in seawater as a stable product of DOM photolysis, biological processes and imported by rainfall.

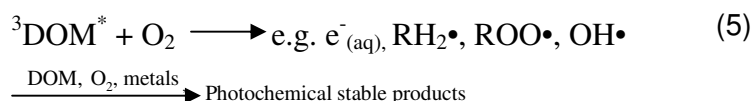
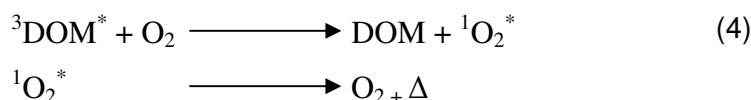
Determined main source for reactive intermediates is the dissolved organic matter (DOM) (Mopper & Zhou 1990, Zhou & Mopper 1990, Takeda et al 2004). Dissolved organic matter is a mixture of very stable, long-chained organic molecules. Despite its function as largest carbon reservoir on earth > 50 % of DOM are uncharacterized. However, the uncharacterized fraction of DOM is the strongest light-absorbing component and plays a dominant role in marine photochemical processes especially in coastal regions (de Mora et al 2000).

Primary reactive intermediates of photochemical oxidation of DOM and estimated concentrations are given in Table 1. In the following we briefly describe the source and reactions of the major reactive transients. Reaction pathways of primary reactive intermediates with acceptor molecules often include formation of secondary reactive intermediates.

Absorption of light leads to the formation of singlet excited state DOM ($^1\text{DOM}^*$). Most of the absorbed energy is dissipated as fluorescent light ($h\nu'$) and heat (Δ), but the $^1\text{DOM}^*$ can also undergo an intersystem crossing (ISC) to its triplet excited state ($^3\text{DOM}^*$) (3).



The dominant energy acceptor molecule during decay of $^3\text{DOM}^*$ is ground state oxygen leading to the formation of excited state singlet oxygen ($^1\text{O}_2^*$), which entirely decays back to the ground state O_2 dissipating energy as heat (4). But, other pathways lead to the formation of reactive intermediates. These pathways are largely unknown and subsequently lead to the formation of photochemical stable products (5) (de Mora et al. 2000).



Intermediate	Estimated concentration (M)
Singlet Oxygen ($^1\text{O}_2$)	$10^{-14} - 10^{-13}$
Hydrated electron ($\text{e}^-_{(\text{aq})}$)	$10^{-17} - 10^{-15}$
Carbon-centred radicals ($\text{RH}_2\bullet$)	$10^{-13} - 10^{-11}$
Organoperoxides ($\text{ROO}\bullet$)	$10^{-14} - 10^{-10}$
Hydroxyl-Radicals ($\text{OH}\bullet$)	$10^{-19} - 10^{-17}$

Table 1: Primary reactive intermediates of photochemical oxidation of DOM and estimated concentrations in sunlit natural waters (modified from de Mora et al. 2000)

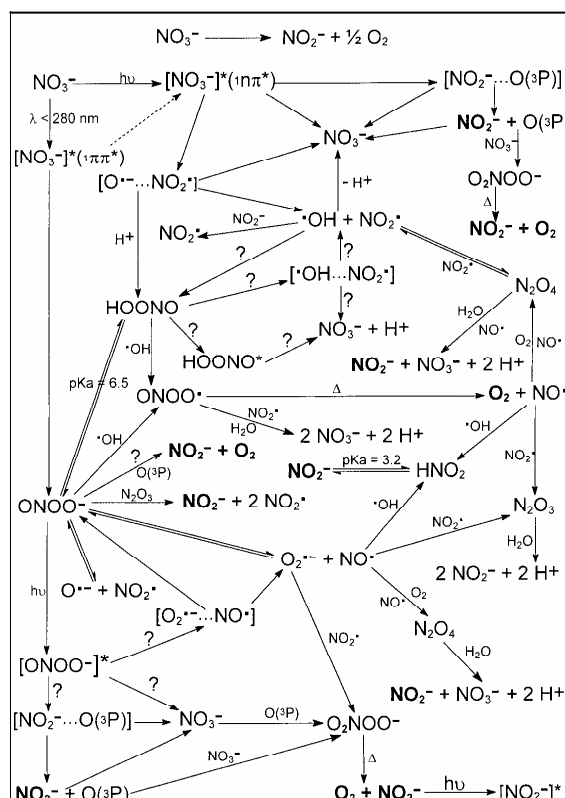
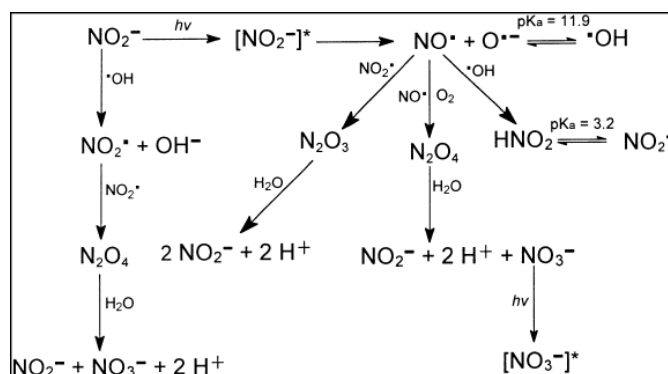
The production of singlet oxygen ($^1\text{O}_2$) is established in natural waters. The major degradation pathway of $^1\text{O}_2$ is quenching by water (Cooper et al. 1989).

Hydrate electron ($\text{e}^-_{(\text{aq})}$) formation has been proven in the laboratory. Electrons form caged ion pairs with $^3\text{DOM}^*$. The majority of caged pairs collapse back to $^3\text{DOM}^*$, while few are ejected and transform into $\text{e}^-_{(\text{aq})}$. The role of $\text{e}^-_{(\text{aq})}$ in reaction with O_2 therefore is minimal, but contributes to the formation of Hydrogenperoxide (H_2O_2) (Cooper et al. 1989).

Origin and fate of Carbon-centred radicals ($\text{RH}_2\bullet$) and organoperoxides ($\text{ROO}\bullet$) is largely unknown due to the unresolved nature of DOM itself. (Cooper et al. 1989, Hoigné et al. 1989).

Due to its high oxidising potential $\text{OH}\bullet$ is by far the most reactive transient species. It reacts at a nearly diffusion controlled rates with most organic substances (Cooper et al. 1989, Hoigné et al. 1989, Buxton et al. 1988).

The reactive transients of DOM photolysis have important functions in the photochemical degradation of DOM and the marine carbon cycle. Reactive transients are short lived and generally cause no harm to organism (Palenik et al. 1991, de Mora et al. 2000). Main sink for e.g. $\text{OH}\bullet$ is DOM itself resulting in the formation of low weight carbonyl compounds (LWC). Such LWC are more accessible for decomposition by micro-organisms (Cooper et al. 1989, Hoigné et al. 1989, de Mora et al. 2000, Pullin et al. 2004). The potential formation of ecotoxicological relevant compounds and their role in the marine environment is unknown for most of the transient intermediates. However, several ecotoxicological relevant reaction products of $\text{OH}\bullet$ with components of seawater are known or can be inferred and are described in detail under chapter 2.2.3.



Figures 4a and 4b: Main reaction pathways and following processes of NO_2^- photolysis and NO_3^- Photolysis (from Mack & Bolton 1999).

The formation of potential eco-toxicological relevant compounds by OH• depends on OH• concentration. Steady state concentrations of OH• in seawater under natural light conditions are generally low (10^{-19} to 10^{-17} M) (Zepp 1987, Zhou & Mopper 1990, Brezonik & Fulkerson-Brekken 1998, Vaughan and Blough 1998, de Mora et al. 2000, Takeda et al. 2004). Photolytic production rate of OH• from DOM is in the range of $3\text{--}6 \times 10^{-12} \text{ Ms}^{-1}$ and $3\text{--}8 \times 10^{-12} \text{ Ms}^{-1}$ including NO_3^- , NO_2^- , and H_2O_2 as sources (Mopper & Zhou 1990, Takeda et al. 2004).

Zhou and Mopper (1990) and Takeda et al. (2004) were able to show, that about 80 % of OH• in surface layer of seawater originated from the photolysis of DOM, the least important sources were NO₃⁻ and H₂O₂ (< 1.5%). However, NO₃⁻ and NO₂⁻ are more important OH• sources in freshwater systems.

H₂O₂ is a ubiquitous compound in natural waters and a comparably stable product of photolysis in natural waters (Avery et al. 2004). It is produced by the recombination of OH• and secondary intermediates of DOM photolysis, introduced by natural rainfall and biological

processes (Avery et al. 2004). Concentrations in natural waters are e.g.: seawater $[H_2O_2] = 0.5 - 14 \mu\text{g/l}$, freshwater $[H_2O_2] = 1 - 30 \mu\text{g/l}$. According to Takeda et al. (2004) the concentration of H_2O_2 in coastal waters is proportional to the intensity of solar irradiation with a maximum of 400 nM on midday in summer resulting in an OH^\bullet production rate of $0.84 \times 10^{-12} \text{ M/s}$.

However, the described mechanisms are all relative to natural daylight including UVA and B. The AquaTriComb™ BWTS uses a LPUV-system emitting monochromatic $UV_{254\text{nm}}$. UVC is absorbed completely in the atmosphere, therefore $UV_{254\text{nm}}$ is not part of natural sunlight. The expected OH^\bullet production during BWT by the AquaTriComb™ BWTS is expected to be much lower than under natural sunlight conditions for several reasons:

- Generation of OH^\bullet is a time dependent process (Mopper & Zhou 1990, Takeda et al. 2004). During BWT in the AquaTriComb™ BWTS irradiation time with $UV_{254\text{nm}}$ is less than a 1 second. Thus, total OH^\bullet produced should be in the range of the photo-production rate.
- NO_3^- and NO_2^- absorbance of UV light is weak between 230 and 300 nm (Oppenländer 2003, chapter 6). Therefore production rate of OH^\bullet from these components should be much lower under $UV_{254\text{nm}}$ irradiation.

2.2.2.2 Formation of OH^\bullet by LFUS

Cavitation serves as a mean to concentrate the diffuse energy of ultrasound into hot spots acting as micro-reactors. As mentioned before, the primary source for radical formation in water is the hot gas phase inside the cavitation bubble where hydroxyl-radicals (OH^\bullet) and hydrogen-radicals (H^\bullet) are generated by sonolysis of water according to equation (6) in equal concentrations. Hydrogen peroxide and hydrogen are formed by recombination of the radicals according to the equations (7) and (8).



As outlined earlier, radical production depends on the US frequency. It is well documented that the frequency has a significant influence on bubble dynamics, including temperature inside the bubble and bubble size (Suslick 1989). However, primary formation of radicals is a relatively slow process with reaction rates in the order of 10^{-4} to 10^{-5} mol/lmin (Mason & Peters 2002).

Radical formation can be detected with different methods. In an indirect test the production of H_2O_2 , resulting from the recombined OH^\bullet (equation 2) is measured with an iodine dosimeter. KI is added to the solution before sonofication and H_2O_2 reacts quickly with I^- and liberates molecular iodine. The yield of iodine can be measured by UV/VIS spectroscopy at 355 nm.

The Fricke-dosimeter uses the oxidation of Fe^{2+} to Fe^{3+} by several ultrasound generated species (OH^\bullet ; H^\bullet). General descriptions of these and further methods like the terephthalate dosimeter or the nitrophenol dosimeter are described elsewhere (Mason & Peters 2002).

Using the mentioned methods several studies comparing the frequency and sonofication time could show an increase of the generation of OH^\bullet with increasing time as well as increasing frequency. Higher frequencies increase the number of free radicals produced due to the increased number of (less violent) cavitation events (Thompson and Doraiswamy 1999, Abu-Hassan et al. 2006).

In a study exploring the sonodegradation of persistent detergents Abu-Hassan et al. (2006) could demonstrate by the detection of H_2O_2 that the generation of radicals in aqueous solution increases during the first 60 minutes of sonification. The concentration of H_2O_2 after 60 minutes was approximately 1400 $\mu\text{g/l}$. Only very little H_2O_2 (<100 $\mu\text{g/l}$) was produced during the first five minutes of sonification.

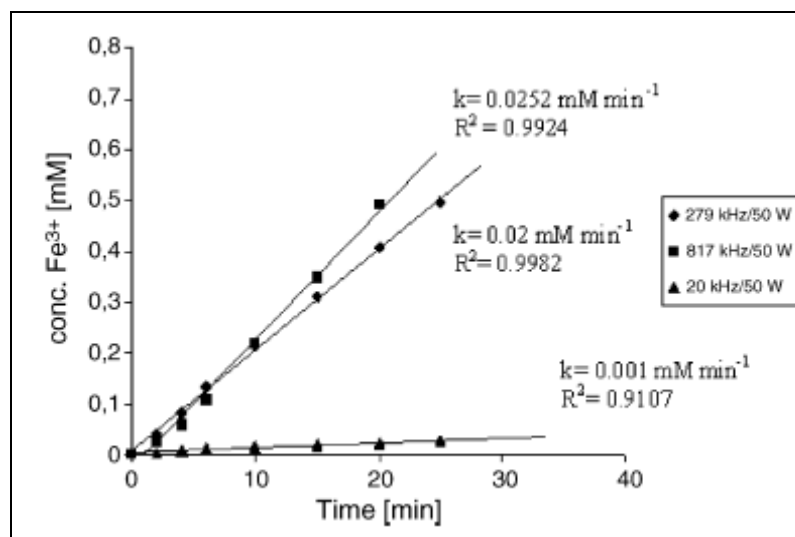


Figure 5: Effect of the frequency on the radical production (measured as Fe^{3+} formation rate) at fixed acoustic power of 50 W (Vajnhandl & Le Marechal, 2007).

Using Fricke-dosimetry Vajnhandl and Le Marechal (2007) could demonstrate a 20-25 fold lower radical formation rate by low frequency US (20 kHz) compared to high-frequency US (279 kHz and 817 kHz). Using 20 kHz with an acoustic power of 50 W the generation of radicals did not increase with sonofication time and the total production rate measured was 0.001 mM/min (Figure 5).

For the application of US in the AquaTriComb™ BWTS it is of crucial importance to use a frequency by which the micro organisms and inorganic accumulations are completely removed and the formation of radicals will be avoided. Results in the mentioned studies indicate that nearly none reactive intermediates are generated using low frequency US (20 kHz) with no processes or sonification during very short times. Hence, the use of low frequency (20kHz) US and very short applications times (< 1s) in ballast-water treatment of the AquaTriComb™ BWTS is recommendable due to nearly none by-product formation (Gavand et al. 2007, Holm et al. 2008).

2.2.3 Other chemicals

Oxidative degradation of organics by OH^\bullet is used in portable and waste water disinfection. Very general, oxidative attack of OH^\bullet leads to the formation of above mentioned carbon centred radicals (RH_2^\bullet) (2.2.2.1, Table 1). The RH_2^\bullet immediately react with dissolved molecular oxygen producing a peroxy radical (R-O-O^\bullet). The R-O-O^\bullet undergoes a vast variety of rearrangements and/or eliminations to form the final oxidation product (R^{ox}). Final oxidation products are ketones, alcohols, aldehydes, molecular oxygen, aliphatic peroxides and H_2O_2 depending on the aliphatic skeleton of the attacked organic (Oppenländer 2003). However, it has been demonstrated that the formation of carbonyls (e.g. aldehydes) at UV doses greater than 400 mJ/cm^2 during wastewater and raw portable water disinfection is very low (Liu et al. 2002)

Due to the unpredictable nature of the compounds potentially formed from DOM degradation in natural seawater by OH^\bullet we focus on compounds where formation is known and which potentially cause a risk to the environment or are regulated in water quality acts (e.g. trichloroacetic acid is a registered herbicide and regulated by the German portable water act, BGBl 2001). Of most environmental concern are H_2O_2 , Trihalomethanes (THMs) and Haloacetic Acids (HAAs) as well as other organic halides (RX).

H_2O_2 occurs naturally in seawater and is formed by photolytic and biological processes or is introduced by rainfall (Avery et al. 2005). H_2O_2 is generated by the recombination of two OH^\bullet radicals:



Natural decay follows photolytic and biological pathways. Half-life of H_2O_2 in oligotrophic seawater estimated from decay rates under dark conditions is in the order of 16 – 224 h. Sea water concentration of H_2O_2 vary over a broad range (0.5 – 14 $\mu\text{g/l}$) depending on solar intensity, biological processes, rain input and the concentration of photolytic degradable DOM. H_2O_2 concentration in oligotrophic Atlantic surface water is about 100 nm (Bermuda triangle, Sargasso Sea) (Avery et al. 2004), while 400 nm H_2O_2 have been measured in coastal waters.

The potential increase of H_2O_2 concentration in different salinities during BWT by the AquaTriComb™ BWTS is shown by water analysis to be below the Level of Quantification.

Formation of THMs, HAAs and RX are common and regulated disinfection by-products (DBPs) during waste and portable water sanitation using chlorine or chlorine species (Oppenländer 2003, Westerhoff et al. 2004, USEPA 2006). DBP formation is known to be insignificant at UV doses below 400 mJ/cm^2 upon subsequent chlorination in portable water sanitation (USEPA 2006). Liu et al. (2002) showed that the formation of THMs and HAAs by chlorination is unaffected by prior UV irradiation with doses less than 1000 mJ/cm^2 . The formation of THMs, HAAs and RX in aqueous solution from halogen species has been described (Oppenländer 2003 chapter 6, Westerhoff et al. 2004). Halogenated by-product formation involves OH^\bullet (after Oppenländer 2003, chapter 6):



Where X^- is a halogen ion (10), HOX^- is hypohalogenic acid (10), X is a halogen atom (11), R is an organic molecule and RX is the final organic halide.

Natural seawater contains organic halogens from anthropogenic input (chemical industry, chlorinated Seawater as cooling agent in power plants, portable water disinfection) and natural sources (reactions of atmospheric organics with reactive halogens, production by algae, and sunlight induced photolysis of DOM). Concentrations of e.g. THM and organic halides measured in the North Sea and the Baltic are in the order of 0.2 – 15 ng/l while composition depends on sampling site (Kuß 1994).

The potential increase of THM, HAA and RX concentration in different salinities during BWT by the AquaTriComb™ BWTS is shown by water analysis to be below the Level of Quantification.

As shown in figure 4b, Nitrite can be produced from Nitrate by photolysis. The yield of the photoreaction of Nitrate to Nitrite is sensitive to both the dissolved inorganic and organic carbon content of natural water (Sharpless et al, 2003). Buchanan et al. (2006) showed that the nitrate concentration of untreated water directly influences the concentration of Nitrite produced as a consequence of UV and vacuum UV (VUV) irradiation. However, various doses of UV and vacuum UV irradiated natural organic matter were deemed non-cytotoxic. Similarly, a conducted Ames test showed no mutagenic response after various doses of both UV and VUV irradiation (Buchanan et al. 2006).

Together with Ammonium (NH_4^+) and Nitrate (NO_3^-), Nitrite (NO_2^-) is the most common ionic (reactive) form of dissolved inorganic nitrogen in aquatic ecosystems. All these ions can be present naturally as a result of atmospheric deposition, surface and groundwater runoff, dissolution of nitrogen-rich geological deposits, N_2 fixation by certain prokaryotes (cyanobacteria with heterocysts, in particular), and biological degradation of organic matter.

2.3 Data on effects on aquatic plants, invertebrates and fish, and other biota including sensitive and representative organisms (G9: 4.2.1.1)

This chapter has the purpose to evaluate the effects of Preparations and its components to the organisms and the environment when released with the treated ballast water or accidentally during the process.

AquaTriComb™ BWTS applies Low Pressure UV (LPUV) lamps emitting monochromatic light at the specific wave length of 254 nm ($\text{UV}_{254\text{nm}}$). At this wavelength, specifically DNA is damaged and the formation of by-products is reduced.

Photons will not persist after the UVC exposure phase. Also OH^\bullet as Relevant Substance has a very short half-life and will not persist outside the BWTS system. Accordingly these two “substances” will be discussed below shortly with regard to their reaction mechanism and reactivity but not with regard to aquatic toxicity.

Nucleic acids and Nucleotides as components of DNA and RNA absorb in the wave length spectrum of 200 – 400 nm with a distinct maxima at 200 and 260 nm. Absorption of photon energy mediates the formation of various photolytic products in DNA and RNA inhibiting gene expression (e.g. base dimers, strand- and double strand breaking, photohydrates). The most important, irreversible and lethal damage arises from the formation of pyrimidine base dimers, which block the translation and transcription of DNA and RNA, impeding replication and protein biosynthesis of micro-organisms (Görner 1994, de Mora et al. 2000). The dimer formation is initiated by an excited state oxygen (Wei et al. 1997, Schreier et al. 2007). It has also been shown that UVC (100 – 280 nm) causes photolytic inactivation of various proteins potentially enhancing the germicidal effect (Chan et al. 2006 and references therein).

Absorption time for a photon by a molecule is in the range of nano- to pico-seconds. The use of UV for water disinfection and treatment (including ballast water treatment) is considered a purely physical process, limited to the time of radiation exposure and producing negligible amounts of by-products (DVGW 2001, USEPA 2006, Umweltbundesamt 2008). Hence no residuals of the photon are to be expected in the treated ballast water.

OH^\bullet -radicals as “Relevant Substance”: Due to its high oxidising potential OH^\bullet is by far the most reactive transient species that is produced in this process. It reacts at a nearly diffusion controlled rates with most organic substances (Cooper et al. 1989, Hoigné et al. 1989, Buxton et al. 1988). Its life time of about 1 nanosecond restricts its process-related appearance to the ballast water treatment phase. No increased concentrations outside the plant are expected.

2.3.1 Environmental toxicity of Other Chemicals - Nitrite

In the case of the AquaTriComb™ BWTS Other Substances, which can theoretically be produced by the applied method as by-products within the process, could be of potential concern. According to chemical analyses, none of the Other Substances, discussed in this dossier, are determined above Levels of Quantification (see discussion of results chapter 5.2) except for Nitrite, where values are above the LoQ both for measurements before and after the treatment process. Investigated Nitrite concentrations before and after treatment process are statistically proven not significantly different (see chapter 5.2), what means the Nitrite values are not generated by the treatment process. Nevertheless in the following chapters we discuss literature data on environmental toxicity for Nitrite.

2.3.1.1 Acute aquatic effects

Because in aquatic ecosystems the NO_2^- concentration usually is much higher (about 4-5 orders of magnitude) than the concentration of its unionized nitrous acid HNO_2 , Nitrite ions are considered to be major responsible for Nitrite toxicity to aquatic animals. The main toxic action of Nitrite on aquatic animals is due to the conversion of oxygen-carrying pigments to forms that are incapable of carrying oxygen, causing hypoxia and ultimately death. In fish, entry of Nitrite into the red blood cells is associated with the oxidation of iron atoms, functional hemoglobin being converted into methemoglobin that is unable to release oxygen to body tissues because of its high dissociation constant. Similarly, in crayfish, entry of Nitrite into the blood plasma is associated with the oxidation of copper atoms, whereby functional hemocyanin is converted into methemocyanin that cannot bind reversibly to molecular oxygen. Water quality criteria within the range 0.08-0.35 mg $\text{NO}_2^- \text{N/l}$ have been proposed to protect sensitive aquatic animals, at least during short-term exposures (Camargo and Alonso, 2006).

The PAN database contains data to the Algae growth inhibition test for 72 hours for *Tetraselmis chuii* and states an EC_{50} of 159 mg/l. The validity to consider this test as an acute test, however, is doubtful, as several algae generations will have grown over this time. Other and more reliable acute data comprise EC_{50} values for crustacea (48 hours), ranging between 27 and 193 mg/l and fish (LC 50) ranging from 11,2 mg/L (*Oncorhynchus mykiss*) to 226 mg/l (*Anguilla anguilla*).

2.3.1.2 Chronic aquatic toxicity

Data on chronic aquatic toxicity are scarce due to the very short life span of the compound which is quickly converted to other nitrogen species in an aquatic environment. Reliable data for chronic toxicity (NOEC) were not available.

2.3.1.3 Endocrine Disruption

An endocrine effect of specifically Nitrate but also Nitrite is being discussed, but no data are available so far (Guillette, 2006). Up to now sodium Nitrite has not been listed as an endocrine substance in the EU prioritization list for endocrine disrupting substances.

2.3.1.4 Sediment toxicity

Under anoxic conditions it can be assumed, that Nitrite is rapidly denitrified to e.g. N_2O .

2.3.1.5 Bioavailability, bioconcentration and food web effects

Accumulation of Nitrite has been shown to depend on the environment and is higher in fresh-water fish, where Nitrite and chloride ions compete for the active branchial Cl^- uptake system.

In seawater, bioaccumulation of NO_2^- in the plasma is much lower (Grosell and Jensen 2000).

2.3.1.6. Overview over toxicological data of Nitrite

Table 2 shows literature data of acute (EC_{50} , LC_{50}) toxicity for the organism groups algae, crustacean and fish for Nitrite. Reliable data for chronic (NOEC) toxicity were not available.

Acute toxicity – EC_{50} , LC_{50}				
Organism group	Duration	mg Nitrite /l	Species	Source
Algae	72 h	159 (EC_{50})	<i>Tetraselmis chuii</i>	PAN Database
Crustacea	48 h	27,1 (EC_{50})	<i>Metapenaeus ensis</i>	PAN Database
		193 (EC_{50})	<i>Penaeus monodon</i>	PAN Database
Fish	96 h	226 (LC_{50})	<i>Anguilla anguilla</i>	PAN Database
		130 (EC_{50})	<i>Danio rerio</i>	PAN Database
		11,2 (LC_{50})	<i>Oncorhynchus mykiss</i>	Kroupova et al. 2008

Table 2: Literature data of acute (EC_{50} , LC_{50}) toxicity for the organism groups algae, crustacean and fish to Nitrite

2.3.1.7 Evaluation of the PNEC

A PNEC of 0,01 mg/l has been determined by Bursch (2003) on the basis of chronic NOEC for 3 trophic levels². This value has been suggested as the result of discussions by the competent authorities of the EU-member states. This level, however, has been critically discussed as the level is strongly dependent on the chloride concentration as well as other factors, and seemed unrealistically low.

The Environmental Quality Standards for Nitrite have been proposed, based on data from Schwoerbel (1991) and addressing the differences in toxicity to aquatic organisms depending on the salinity of the ambient water:

0-3 mg Cl^-/l	→ 33 $\mu\text{g}/\text{l}$ NO_2^-
<3 – 7.5 mg Cl^-/l	→ 164 $\mu\text{g}/\text{l}$ NO_2^-
<7.5 - 15 mg Cl^-/l	→ 296 $\mu\text{g}/\text{l}$ NO_2^-
<15 - 30 mg Cl^-/l	→ 394 $\mu\text{g}/\text{l}$ NO_2^-
>30 mg Cl^-/l	→ 493 $\mu\text{g}/\text{l}$ NO_2^-

2.4 Data on mammalian toxicity (G9: 4.2.1.2)

In the case of the AquaTriCombTM BWTS Other Substances, which can theoretically be produced by the applied method as by-products within the process, could be of potential concern. According to chemical analyses, none of the Other Substances, discussed in this report, are produced above Level of Quantification (see discussion of results chapter 5.2) except for Nitrite, where values are above the LoQ both for measurements before and after the treatment process. Investigated Nitrite concentrations before and after treatment process are statistically proven not significantly different, what means the Nitrite values are not generated

² Derivation of the PNEC is documented in literature cited in Bursch (2003).

by the treatment process. Nevertheless in the following chapters we discuss literature data on mammalian toxicity conditions for Nitrite.

Information is taken from the background document for “development of WHO Guidelines for Drinking water quality: Nitrate and Nitrite in Drinking water, WHO/SDE/WSH/07.01/16, WHO 2007”.

2.4.1 Acute toxicity

The major biological effect of Nitrite in humans is its involvement in the oxidation of normal Hb to metHb, which is unable to transport oxygen to the tissues. The reduced oxygen transport becomes clinically manifest when metHb concentrations reach 10% of normal Hb concentrations and above; the condition, called methaemoglobinaemia, causes cyanosis and, at higher concentrations, asphyxia. The normal metHb level in humans is less than 2%; in infants under 3 months of age, it is less than 3% (WHO 2007).

In a 13-week study in which Nitrite was given to rats in drinking-water, a dose-related hypertrophy of the adrenal zona glomerulosa was observed at all dose levels (100, 300, 1000, or 3000 mg of potassium Nitrite per litre). Increased metHb levels were seen only in the highest dose group (Til et al., 1988). FAO/WHO (1995) concluded that the NOEL in this study was 100 mg of potassium Nitrite per litre (equivalent to 5.4 mg/kg of body weight per day expressed as Nitrite ion), because the hypertrophy seen at this dose was not significantly different from the controls.

2.4.2 Effects on Skin and Eye

No effects on skin or eyes have been reported.

2.4.3 Repeated dose Toxicity

No repeated dose toxicity has been reported.

2.4.4 Chronic toxicity

One of the long-term effects of Nitrite reported in a variety of animal species is vitamin A deficiency; this is probably caused by the direct reaction of Nitrite with the vitamin. The most important effects reported in long-term animal studies were an increase in metHb level and histopathological changes in the lungs and heart in rats receiving Nitrite in drinking-water for 2 years. The LOAEL, which gave a metHb level of 5%, was 1000 mg of sodium Nitrite per litre; the NOEL was 100 mg of sodium Nitrite per litre, equivalent to 10 mg of sodium Nitrite per kilogram of body weight per day (or 6.7 mg/kg of body weight per day expressed as Nitrite ion) (Speijers et al., 1989).

2.4.5 Developmental and reproductive toxicity

Nitrite appeared to cause fetotoxicity in rats at drinking-water concentrations equivalent to 200 and 300 mg of sodium Nitrite per kilogram of body weight per day, causing increased maternal metHb levels. However, after similar doses in feed in other studies, no embryotoxic effects were observed in rats. In a reproductive toxicity study in guinea-pigs at dose levels of 0, 50, or 60 mg of sodium Nitrite per kilogram of body weight per day given by subcutaneous injection, fetal death followed by abortion occurred at the highest dose level. Teratogenic effects were not observed in reported studies in mice and rats (Speijers et al., 1989; FAO/WHO, 1996).

2.4.6 Carcinogenicity and mutagenicity

Nitrite is mutagenic and can cause morphological transformations in in vitro systems; mutagenic activity was also found in a combined in vivo–in vitro experiment with Syrian ham-

sters. The results of in vivo experiments were controversial (Speijers et al., 1989; FAO/WHO, 1996).

At lower Nitrite levels, tumour incidence potentially induced by N-nitroso compounds, resembled those of control groups treated with the nitrosatable compound only. On the basis of adequately performed and reported studies, it may be concluded that Nitrite itself is not carcinogenic to animals (Speijers et al., 1989; FAO/WHO, 1996, 2003a).

2.4.7 Toxicokinetics

No data on toxicokinetics are available.

2.5 Data on environmental fate and effect under aerobic and anaerobic conditions (G9: 4.2.1.3)

In the case of the AquaTriComb™ BWTS Other Substances, which can theoretically be produced by the applied method as by-products within the process, could be of potential concern. According to chemical analyses, none of the Other Substances, discussed in this report, are produced above Level of Quantification (see discussion of results chapter 5.2) except for Nitrite, where values are above the LoQ both for measurements before and after the treatment process. Investigated Nitrite concentrations before and after treatment process are statistically proven not significantly different, what means the Nitrite values are not generated by the treatment process. Nevertheless in the following chapters we discuss literature data on environmental fate and effect for Nitrite.

2.5.1 Nitrite

Together with Ammonium (NH_4^+) and Nitrate (NO_3^-), Nitrite (NO_2^-) is the most common ionic (reactive) form of dissolved inorganic nitrogen in aquatic ecosystems. All these ions can be present naturally as a result of atmospheric deposition, surface and groundwater runoff, dissolution of nitrogen-rich geological deposits, N_2 fixation by certain prokaryotes (cyanobacteria with heterocysts, in particular), and biological degradation of organic matter. Nitrite is an important nutrient within the nitrogen cycle which is depicted below.

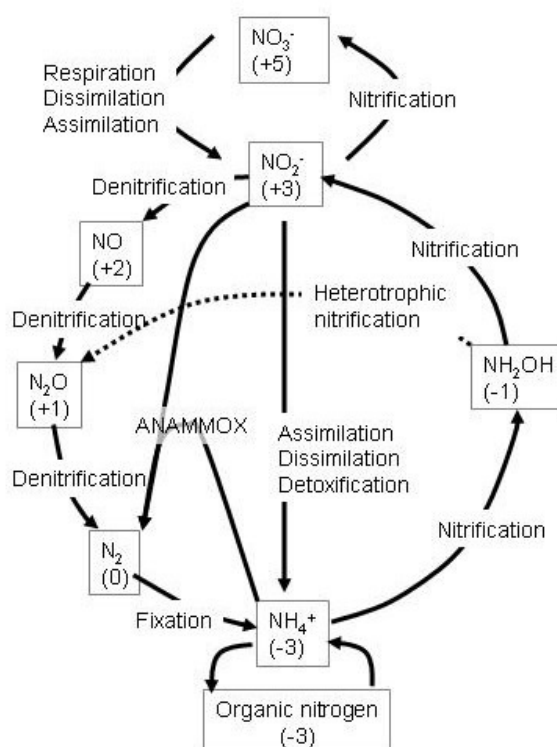


Figure 6: The biological nitrogen cycle. Figures in parentheses denote the nitrogen oxidation state
ANAMMOX: anaerobic oxidation of ammonia with Nitrite (redrawn from Richardson (2000):
Bacterial respiration: a flexible process for a changing environment. Microbiology 146: 551–571, modified in Heise (Ed. 2007)).

2.5.1.1 Modes of degradation

Typical concentration ranges of Nitrite in seawater have been stated to be 0.01 to 5 µg at/l (corresponding to 0.46 to 230 µg NO₂⁻/l (Parsons et al, 1988). Nitrite as an essential element of the nitrogen cycle is involved in a number of aerobic and anaerobic processes. Under oxic conditions, e.g. in the water column or in the oxidised upper sediment layer, chemolithotrophic bacteria, that build organic matter from CO₂, use ammonia and Nitrite (NO₂⁻) as electron donors in a process called nitrification, which yields energy for the organisms. The complete oxidation from ammonia to nitrate (NO₃⁻) is carried out by two different groups of “nitrifying bacteria” that act in concert: Nitrosomonas and Nitrobacter. Nitrogen compounds are removed from the system by denitrification, which occurs under anaerobic conditions: Nitrate and Nitrite act as electron acceptors during anaerobic respiration. The nitrogen-compounds are finally reduced to gaseous compounds N₂ or N₂O. This process is the main process by which gaseous N₂ is formed biologically.

2.5.1.2 Bioaccumulation and persistence

Nitrite under normal “stable” environmental conditions is a transient inorganic nitrogen-compound which is quickly transformed by oxidation or reduction processes (see 2.5.1). Under conditions of unbalanced nitrification, due to anthropogenic activities, problems may be created and are described in chapter 2.3.1. Clark et al. (2007) showed with samples from the North Atlantic Ocean, that Nitrite turnover rates due to ammonium and Nitrite oxidation can be highly variable in oligotrophic waters, ranging from <1 day to > 10 days. Influential factors that regulate the activity of nitrifying bacteria and, thus, the nitrification rates in general, could comprise ammonium-availability, pH, temperature, oxygen concentration, competition for NH₄, and organic carbon availability (Strauss, Dissertation 2000). Hence, concrete assumptions on the persistence of Nitrite are not possible, other than it is very little persistent when compared to non-nutrient compounds.

Nitrite can accumulate in freshwater fish, as it competes with chloride ions for the active Cl⁻-uptake mechanisms. Since the concentration of chloride ions in freshwater is low, presence of Nitrite can lead to NO₂-accumulation (Grosell & Jensen, 2000). In seawater, the much higher chloride concentration limits the uptake, and hence leads to low uptake of Nitrites from surrounding water. Kroupova et al. (2008) found elevated Nitrite levels in the plasma of fish (rainbow trout) exposed to concentrations of 1 mg/l NO₂⁻ and greater.

2.5.1.3 Reaction with organic matter

Nitrite does not react with organic matter in a relevant way.

2.5.1.4 Potential Physical Effects on Wildlife and Benthic Habitats

No physical effects on wildlife and benthic habitats are assumed.

2.5.1.5 Potential Residues in Seafood

Of potential concern with regard to contamination of food with nitrogen compounds is the formation of nitrosamines which are formed in smoked fish products and in the human stomach as the result of the simultaneous presence of secondary amines and Nitrite. Most concern, however, seems to be directed towards the use of nitrogen compounds as preservatives, rather than their uptake by humans from fish which had accumulated Nitrites. As the

knowledge on Nitrite accumulation is fairly new and results so far have been very variable, more research seems to be necessary in this respect.

2.6 Physical and chemical properties for the Preparations, Active Substances and treated ballast water (G9: 4.2.1.4)

Physical / Chemical Property	Active Substance: Photon	Relevant Chemical: OH-Radical	Other Chemical: Nitrite	Treated Ballast water
CAS Nr.	n.a.	3352-57-6	14797-65-0	
Molecular weight [g/mol]	n.a.	17.00734	46	
Melting point (°C)				
Boiling point (°C)				
Density				
Vapour pressure				
Water solubility				
Dissociation constant (pK _a)				
Henry's law constant				
Log K _{ow}				
Oxidation potential				
pH in solution			basic	
Corrosivity to material				
Reactivity to container material				
Autoignition temperature (°C)				
Explosive properties				
Oxidizing properties				
Surface tension				
Viscosity				
(Thermal) stability and break-down product				
Other physical and chemical properties				

Table 3: Physical and chemical properties for Active Substance (Photon), Relevant Chemical (OH Radical) and Other Chemicals

(n.a.: not available, grey column 2 and 3: due to the transient existence, no data are available, column 5: data not available, column 4 Nitrite: no information possible, as it is an ion, all information would refer to the salt, whereby the different compounds would differ strongly depending on the cation, Data from Rippen (2005))

2.7 Analytical methods at environmentally relevant concentrations (G9: 4.2.1.5)

In chapter 2.2 the photon (UV-C radiation) and cavitation bubbles generated by the AquaTriComb™ BWTS have been identified as responsible for the inactivation of organisms, which in turn may result in OH-radicals. OH-radicals are extremely short-lived measured in nanoseconds, thus detection by conventional analytics is not feasible. Reactive effects of OH-radicals may result in reactive by-products like ozone, hydrogen peroxide or hyper bromate. Other possible OH-radicals related by-products are THMs, LHKWs, HAAs, Acetonitrils or Bromophenols. These by-products have been analysed by the laboratories IBEN GmbH (Bremerhaven) and Dr. Kaiser & Dr. Woldmann (Hamburg and Gelsenkirchen).

Basic Approval GloEnPatrol MEPC 57/2/4	GESAMP-List MEPC 58/2/7	UBA-List	Basic Approval AquaTriComb™	Formula	Analyzed
AOX	AOX		AOX	AOX	Yes
	EOX		EOX	EOX	Yes
		Nitrite (NO ₂) ⁻	Nitrite (NO ₂) ⁻	NO ₂	Yes
		Cl ₂	Cl ₂	H ₂ O ₂	Yes
		Hydrogen peroxide	Hydrogen peroxide	H ₂ O ₂	Yes
		Ozone	Ozone	O ₃	Yes
		Hyperbromate	Hyperbromate	BrO ⁻	Yes
Chloroform	Chloroform	Chloroform	Chloroform	CHCl ₃	Yes
Bromoform	Bromoform	Bromoform	Bromoform	CHBr ₃	Yes
Dibromochloromethan	Dibromochloromethan	Dibromochloromethan	Dibromochloromethan	CHBr ₂ Cl	Yes
Dichlorobromomethan	Dichlorobromomethan	Dichlorobromomethan	Dichlorobromomethan	CHCl ₂ Br	Yes
Monochloroacetic acid			Monochloroacetic acid	C ₂ H ₃ ClO ₂	Yes
Dichloroacetic acid			Dichloroacetic acid	C ₂ H ₂ Cl ₂ O ₂	Yes
Trichloroacetic acid			Trichloroacetic acid	C ₂ HCl ₃ O ₂	Yes
Monobromoacetic acid	Monobromoacetic acid	Monobromoacetic acid	Monobromoacetic acid	C ₂ H ₃ BrO ₂	Yes
	Dibromoacetic acid	Dibromoacetic acid	Dibromoacetic acid	C ₂ H ₂ Br ₂ O ₂	Yes
	Tribromoacetic acid	Tribromoacetic acid	Tribromoacetic acid	C ₂ HBr ₃ O ₂	Yes
Bromochloroacetic acid	Bromochloroacetic acid		Bromochloroacetic acid	C ₂ H ₂ BrClO ₂	Yes
Dibromochloroacetic acid	Dibromochloroacetic acid		Dibromochloroacetic acid	C ₂ HBr ₂ ClO ₂	Yes
	Bromodichloroacetic acid		Bromodichloroacetic acid	C ₂ HBrCl ₂ O ₂	Yes

Basic Approval GloEnPatrol MEPC 57/2/4	GESAMP-List MEPC 58/2/7	UBA-List	Basic Approval AquaTriComb™	Formula	Analyzed
	1,2- dibromoethane		1,2- dibromoethane	C ₂ HBr ₂	Yes
	1,2,3-trichloropropane		1,2,3-trichloropropane	C ₃ HCl ₃	Yes
	2-chlorotoluene		2-chlorotoluene	C ₇ H ₇ Cl	Yes
	4-chlorotoluene		4-chlorotoluene	C ₇ H ₇ Cl	Yes
1,2-dibromo-3-chloropropane	1,2-dibromo-3-chloropropane		1,2-dibromo-3-chloropropane	C ₃ H ₅ Br ₂ Cl	Yes
	1,2,3-tribromobenzene		1,2,3-tribromobenzene	C ₆ H ₃ Br ₃	Yes
1,1,1-Trichlorethan			1,1,1-Trichlorethan	C ₂ H ₃ Cl ₃	Yes
Carbon tetrachloride			Carbon tetrachloride	CCl ₄	Yes
Tetrachlorethen			Tetrachlorethen	C ₂ Cl ₄	Yes
	Monobromoacetonitrile	Monobromoacetonitrile	Monobromoacetonitrile	C ₂ H ₂ BrN	Yes
	Dibromoacetonitrile		Dibromoacetonitrile	C ₂ HBr ₂ N	Yes
	Bromochloroacetonitrile		Bromochloroacetonitrile	C ₂ Br ₃ N	Yes
	2,4-dibromophenol		2,4-dibromophenol	C ₆ H ₄ Br ₂ O	Yes
	2,6-dibromophenol		2,6-dibromophenol	C ₆ H ₄ Br ₂ O	Yes
	2,4,6-tribromophenol	2,4,6-tribromophenol	2,4,6-tribromophenol	C ₆ H ₃ Br ₃ O	Yes

Table 4: List of substances identified as possible by-products and analysed by Aquaworx

In Table 4 three different lists identify disinfection by-products (column 1 to 3), non-conformity between the lists is marked "yellow":

- Column 1 as given in MEPC 57/2/4 is a combination of technologies similar to AquaTriComb™ BWTS
- Column 2 according to GESAMP Ballast Water Group, MEPC 58/2/7
- Column 3 according to recommended list of possible by-products as given by German Federal Environment Agency (Umweltbundesamt Deutschland, UBA)

Water samples were analysed regarding the substances from all lists as shown in column 4. Full data of results for analysis of samples are shown in Tables A1 – A3 in Annex A.

The following Table 5 shows by three laboratories analysed Other Chemicals including Levels of Quantification and identification numbers of the standardised methods.

Parameter	Level of Quantification	Methods	Certified laboratories
Nitrite (NO ₂)	0,007 mg/l	DIN EN 26 777 1993-04	Labor IBEN
AOX	0,02 mg/l	DIN EN 1485: 1996-11	Labor IBEN
EOX	0,002 mg/l	DIN 38141-S17 1989-11	Labor IBEN
THM: Chloroform Bromoform Dibromochloromethan Dichlorobromomethan	0,02 µg/l	EN ISO 10301 1997-04	Labor IBEN
LHKW 1,2- dibromoethane 1,2,3-trichloropropane 2-chlorotoluene 4-chlorotoluene 1,2-dibromo-3-chloropropane 1,2,3-tribromobenzene 1,1,1-Trichlorethan Carbon tetrachloride Tetrachlorethen	0,02 µg/l	EN ISO 10301 1997-04	Labor IBEN
HAA: Monochloroacetic acid Dichloroacetic acid Trichloroacetic acid Monobromoacetic acid Dibromoacetic acid Tribromoacetic acid Bromochloroacetic acid Dibromochloroacetic acid Bromodichloroacetic acid	1,0 µg/l	DIN 38407 F25	Laboratory Dr. Kaiser & Dr. Woldmann, Hamburg
Bromophenols: 2,4-Dibromophenol 2,6-Dibromophenol	0,01 µg/l	GC-MS after derivatisation and extraction	Labor IBEN
2,4,6-Tribromophenol	0,04 µg/l	GC-MS after derivatisation and extraction	Labor IBEN
Acetonitrils: Monobromoacetonitril Dibromoacetonitril Bromchloroacetonitril	1,0 µg/l	US EPA Method 551.1	Laboratory Dr. Kaiser & Dr. Woldmann, Gelsenkirchen
TRO: Cl ₂ , H ₂ O ₂ , O ₃ , BrO	All substances: 0,05 mg/l	EN ISO 7393-1 2000-04 (G4-2)	Labor IBEN

Table 5: By three certified laboratories analyzed possible by-products including Levels of Quantification and certified methods.

Certified standards are among the samples at the beginning of every analytical run. Every method is also included in periodic participation on external laboratory tests except for Bromophenols, see below.

Levels of Quantification:

According to the report of the seventh meeting of the GESAMP Ballast Water Working Group in Annex 5 (MEPC 58/2/8) Levels of Quantification (LoQ) for THMs and HAAs for surface waters are recommended as 0,01 – 0,05 µg/l. The laboratories involved in our analysis were able to reach LoQs for THM, LHKW and Bromophenols of 0,02 µg/l (Labor IBEN, Bremerhaven), which meets the recommended range. In the case of the HAAs experts of the laboratories have spent considerable effort to find methods or laboratories, which are able to meet the recommended LoQs. The effort to find a solution also included the attempt, to establish and optimise a standardised analytical method regarding this special demand. As the best result the laboratory Dr. Kaiser & Dr. Woldmann (Hamburg) was able to reach a LoQ for HAAs with 1 µg/l. Experts of the laboratory explain the background of the applied analytical method and the reason why the LoQ of 0,01 – 0,05 µg/l could not be reached (see below analyse method of HAAs and Annex D: Description of method for determination of HAA, Laboratory Dr. Kaiser & Dr. Woldmann, Hamburg).

Analyse methods:

The analyses of AOX/EOX have been carried out according to DIN EN 1485: 1996-11 and DIN 38141-S17 1989-11 with a coulometer of company Umcate. The parameters are so called summation parameter. They detect certain matters in their complexity and allow for interpretations which are important with regard to the advanced analysis strategy and to the plausibility control. As to AOX and EOX it is the sum of the halogenated absorbable and extractable compounds within the probe. The measures to assure quality for such analyses are defined by DIN. That is besides the blank value of the instrument, the blank value is carried out for the analysis including a regular calibration by means of external standards. For the day-to-day control a control standard is analysed and control readings shall detect methodical problems. Further for AOX regular participation of interlaboratory tests is carried out.

Lightly volatile halogenated hydrocarbons and Trihalogenmethanes has been analysed according to DIN EN ISO 10301 1997-04 with a gas-phase chromatograph with mass spectrometric detection and headspace sampler of Messrs. Agilent. The advantage of detection with a mass spectrometer is the definite identification and classification of the detected substance. The application of the SIM method, which accounts for the specific masses of the detected substances only, allows for very small LoQ. For these parameters the laboratory also regularly participates in interlaboratory tests. The quality assurance methods for these analyses are determined by DIN. That is besides the blank value of the instrument, the blank value is carried out for the analysis including a regular calibration by means of external standards. For the day-to-day control a control standard is analysed and control readings shall detect methodical problems.

Nitrite is analysed according to DIN EN 26 777 1993-04 with a photometric procedure. At a specific wave length the colour reaction is detected with a reagent. The procedure for quality assurance is according to DIN and includes a daily calibration, a blank value as well as control standards which are documented on control charts.

The analysis of ozone, hydrogen peroxide and hyper bromate has been done in-situ with the method for free chlorine as the sum of the existing oxidants in water. A mobile photometer has been applied which allows for the measurement of the colour intensity as direct reaction with N,N-Diethyl-1,4-phenyldiamin and formation of a reddish compound at pH 6.2 to 6.5 according to EN ISO 7393-1; 2000-04 (G4-2).

Bromophenols were analysed with a gas-phase chromatograph with mass spectrometric detection and autosampler of the company Agilent. Analysis is done after derivatisation as methyl ester. The advantage of detection via mass spectrometer is to found in the definitely identification and in the clear classification of the investigated substances. By means of using the SIM method, which considers only specific masses of analysed substances, very low LoQs can be achieved. For this parameters the laboratory can not take part in interlaboratory tests (ring tests), because these parameters are until now not implemented in ring tests. Quality control measures for this analysis include beside blind values of the instrument, blind values for the method also permanent calibration with external standards. For the daily control a control standard is analysed.

Difficulties arose to find a laboratory to analyse halogenated Acetonitrils. Analysis of these substances are very seldom asked for, and therefore laboratories have rarely established respective certified analytic methods. The laboratory Dr. Woldmann & Dr. Kaiser (Gelsenkirchen) analysed Acetonitrils according to the US EPA method 551.1. With regard to the sound solubility of the Acetonitrils the salt sodium sulphate was added (shifting of the solution equilibrium) and subsequent extracted with MTBE. The extract will be concentrated and then analysed with GC/MS. All three Acetonitrils are measured with a LoQ of 1 µg/l.

Determination of HAA was performed following the guideline EN ISO 23631:2006. The analytical range was within 0.5-10 µg/l according to the standard solutions employed, depending on the matrix of the samples, respectively. Our estimated limit of quantitation was 1 µg/l, which is appropriate for the analytical range stated above. Description of method and analytical constraints: 200 ml of aqueous test solution is adjusted to pH 1 and extracted after addition of 20g sodium chloride with 20 ml MTBE. Subsequently, the organic extract is removed and concentrated to 1 ml. After derivatisation of the analyte with diazomethan, concentrations were assessed by means of GC-ECD. However, since the compounds under study are very polar extraction is rather difficult and will eventually be not complete. Furthermore, it will not be possible to decrease the limit of quantitation by increasing the sample volume thus leading to higher concentrations of the analyte in the organic extract. This is due to the fact the matrix will also be concentrated in this way, leading to unfavourable disturbances of the detection by GC-ECD.

2.8 Quality control / quality assurance (G9: 4.2.4)

For all three laboratories the Analytic Quality Assurance (AQS) is of utmost importance. It is the prime aim to deliver reliable analytic results of defined quality. Therefore one of their main targets is the quantitative assessment of all applied analyse methods, if necessary the improvement of these methods, and to ensure and to document the achieved quality throughout the analytic routine.

To meet this challenging target a quality management system (QM) is implemented. This system governs all quality related routines and provides the pre-conditions for continuous quality improvement according to DIN EN ISO 17025 and "Good Laboratory Practice" (GLP).

To comply with the high demands regarding analyses in the water pertaining enforcement the existing AQS measures have been aligned to the "Rahmenempfehlungen der Länderarbeitsgemeinschaft Wasser (LAWA) für die Qualitätssicherung bei Wasser-, Abwasser- und Schlammuntersuchungen" (basic recommendations of the working group water for the quality assurance of water, waste water and sludge analyses). On this basis the laboratory IBEN is accredited according to DIN EN ISO 17025 and holds several other concessions for legally regulated sectors. That means that in addition to internal quality assurance external controls in form of mandatory and periodic interlaboratory tests have to be carried out. This in turn guarantees the permanent control of services. Participation in interlaboratory tests is obliga-

tory by means of the accreditation, that is that these tests have to be performed to maintain the accreditation.

3 USE OF ACTIVE SUBSTANCE(S)

Although the AquaTriComb™ does abstain from any Preparations the highly efficient combination of ultraviolet radiation and ultrasonic oscillation generates photons and cavitation bubbles. Nor photon or cavitation bubbles are residual in the treated ballast water and thus have no toxicological effects upon discharge into the environment.

The OH radical, which can be generated by photons and cavitation bubbles reacts at nearly diffusion controlled rates with organic compounds and exists for about 10^{-9} seconds. Therefore OH• is considered not resident in the treated ballast water and causes no harm to the environment upon discharge.

The OH radical related by-products are discussed above in chapter 2, and data on analysed water samples showed, none of the investigated substances are generated by the treatment process regarding to the applied Levels of Quantitation. For this risks to human health and / or to the environment can be demonstrably excluded.

3.1 Operational Overview & Process Description

The AquaTriComb™ BWTS will be installed in line behind the ballast water pumps with a bypass pathway. Both, ballast water intake flows as well as de-ballasting flows will be directed via the whole treatment system.

Two of the three MicroSintFilter modules are permanently active in the filtration process, the third module is in cleaning and stand-by mode.

Pressure difference in front of and behind the treatment system will be approximately 1 bar, depending on the contamination of the water. From the system the ballast water is directed into the ballast tanks and via the ballast water pump(s) into the sea, respectively.

3.2 System Monitoring & Control, Crew Interaction

The AquaTriComb™ treatment plant is fully automated and completely self-contained with electronic steering, switch board, and control panel including emergency shut-off device. The plant can be readily pre-mounted in accordance to the ship's specifics for connection to the shipboard power supply system.

The monitoring and control devices include flow meters, pressure transmitter, electronically driven actuator valves with manual setting option, and sample ports. Also operating hours counter and malfunction writer will be installed (data logging).

Depending on the grade of automation of the existing ballast water system, typically the plant requires no additional action by the crew or alterations of current ballast water procedures. If any, minor modifications to ballasting procedures are ship specific and will be carefully considered during system engineering and installation.

3.3 System Requirements

Power requirements: the power requirements for the AquaTriComb™ treatment plant with 250 m³/h are: approximately 15.3 kW/h 50/60 Hz, rotary current.

Space requirements: The treatment plant is designed as a modular system – all single filter modules and the UVC-reactor can be installed independently. For this reason in the case of refitting ships with AquaTriComb™ BWTS the existing space can be optimally used. The footprint of a compact system equals about 3 to 4 m².

As the MSF modules as well as the UV-reactor are vertically installed sufficient top space has to be foreseen for exchange of filter module and US oscillators, respectively.

Personnel requirements: the treatment plant is designed to need minimum input from the crew. The crew member performs ballasting and de-ballasting procedures as normal and the AquaTriComb™ starts operations after activation of switch-on device. Further, Aquaworx is offering a training unit to the key shipboard personnel to get familiar with the system.

Maintenance requirements: the ultrasonic tube oscillators need to be exchanged at the earliest after approximately 16,000 and 20,000 operating hours, the low pressure mercury germicidal lamps after about 12,000 operating hours. All other system components do not need any extra maintenance and will be integrated into the routinely applied shipboard plant maintenance schedule. Depending on the ship and the ship's trade a maintenance contract will be signed considering periodic reviews and other specifics.

Handling of waste and replaced parts of the treatment system: during the treatment process no liquid or solid waste appears. Only in the case of completed operating hours, or broken, or out of order UVC lamps, the glass tubes of the lamps have to be changed and disposed. In case of broken glass no hazard appear to the ship crew, because the mercury is as amalgam accumulated as a thin layer on a special spot the inner glass tube. Broken glass can be disposed on board similar to other glass waste. In case of a hole lamp be removed from the reactor, the lamp should be kept on board for recycling by Aquaworx or by the lamp manufacturer.

3.4 System Locations

The AquaTriComb™ BWTS can be located in any suitable and convenient location dependent on the ship's design. The naval architects and marine engineers of Aquaworx will consider and discuss with the client to keep engineering for the integration of the BWTS at a low level, to not interfere with normal cargo operations and required crew activities, and to look to placement opportunities next to the ballast water pumps to minimize the piping length.

3.5 Operational Safety Features and Alarms

As not otherwise permissible and acceptable in the shipping industry, all system components will be of maritime standard type and will have the appropriate approval of the classification society and / or relevant regulatory authority.

No rotating parts or other physical hazards are originated by the AquaTriComb™ BWTS; hazards from chemicals or other Active Substances are excluded.

At least following alarms will be indicated at the BWTS switchboard:

- UV-reactor operational readiness after approx. 5 minutes warm-up phase after switch on (red to green)
- BWTS in by-pass mode (red)
- General mal function (red)

These alarms may also be indicated at the Engine Control Room (ECR), the Cargo Control Room (CCR) and at the bridge, or a common alarm will be installed there.

An emergency shut-off device will be installed at the BWTS and at the ECR.

3.6 Procedures and Management Measures

The operation of the AquaTriComb™ BWTS is to be integrated into the Ship Safety Manual (SMS) as an integral part of the ISM³ documentation.

That is, a procedure has to be developed based on the AquaTriComb™ BWTS Guidelines for the proper operation of the treatment plant. This procedure also describes the service and maintenance intervals and regular preventive maintenance measures (routinely check of sea chest, piping corrosion and related shipboard routines).

3.7 Evaluation of Management Measures

Preventing exposures and emergency situations starts with proper engineering and installation of the AquaTriComb™ BWTS onboard the ship. The management measures discussed above consider location, training and handling of the plant. In connection with the risk assessment these measures are considered to be adequate to avoid uncontrolled or emergency situations and to operate the ballast water treatment plant in a safe manner.

4 MATERIAL SAFETY DATA SHEETS (G9:4.2.7)

Since Material Safety Data Sheets (MSDS) for the Relevant Chemical OH radical does not exist, MSDS of several investigated Other Chemicals can be found in Annex C.

5 RISK CHARACTERIZATION

In this chapter, the information, displayed in the foregoing chapters concerning hazard identification, exposure assessment and dose-response assessment are summarized in terms of risk assessment.

5.1 Screening for persistence, bioaccumulation & toxicity (G9:5.1)

Photons and cavitation bubbles as well as hydrogen radicals as Relevant Substance have a very low life span of less than nanoseconds (see chapter 2.3.1) and therewith are neither persistent, nor do they bioaccumulate or induce toxic effects outside of the direct treatment chamber. Of potential concern are Other Substances, which can theoretically be indirectly produced by the applied method as reaction products within the process. Whether the statistic results of measured Nitrite values showed, the treatment process is not responsible for detected Nitrite values, however the risk characterization will focus on Nitrite.

5.1.1 Persistence (G9: 5.1.1.1)

Nitrite is a nutrient and either nitrified or denitrified quickly – depending on whether aerobic or anaerobic conditions prevail. A half life of 10 minutes has been estimated.

5.1.2 Bioaccumulation (G9: 5.1.1.2)

Bioaccumulation of Nitrite by freshwater fish is higher than by marine fishes because Nitrite competes with chloride for uptake channel processes. No bioaccumulation factor is available.

5.1.3 Toxicity (G9: 5.1.2.3)

In general, few studies of chronic toxicity are considered to be reliable, and often documentation of experimental set ups is poor.

Information on acute toxicity is more abundant.

³ International Safety Management (ISM) Code: International Code for the Safe Operation of ships and for Pollution Prevention, SOLAS chapter IX

Toxicity of Nitrite to fish even occur at natural concentrations or when nitrification becomes unbalanced due to anthropogenic activities. The toxicity of Nitrite depends on a large number of factors, the most important being water chemistry and especially chloride concentration. Data for acute toxicity are shown in Table 2.

5.1.4 PBT Criteria (G9: 6.4.1, Table 1)

In Table 6 the PBT criteria (Persistence, Bioaccumulation, Toxicity) are shown for Nitrite. Compared with data from G9: *Table 1: Criteria for identification of PBT substances* these results show, that persistence and bioaccumulation rates for the selected substances do not exceed the criteria from Table 1 (G9).

Other substance	Persistence	Bioaccumulation	Toxicity
Nitrite	Turnover has been approximated to be less than a day to more than 10 days (latter in oligotrophic environments).	No BCF has been determined	Data for acute toxicity are shown in table 2

Table 6: Summary of persistence, bioaccumulation and toxicity criteria for Nitrite

5.2 Evaluation of the treated ballast water (G9: 5.2)

To evaluate the impact of ballast water treatment on the production of Other Substances samples were analysed chemically before and after the treatment process.

Test medium	Salinity (PSU)
Freshwater	0
Brackish Water	18,9 – 19,5
Saltwater	31,6 – 33,1

Table 7: Range of salinities during sampling investigating by-products with temperature ranges from 16,1 to 17,8°C.

Treatments were carried out at 3 different salinities (Table 7) and with 2 to 3 parallels in several runs (2 to 4) each before (pre) and after (post) treatment. All results of analysed substances are listed in Tables A1 to A3 in Annex A. All TRO, HAA, THM, LHKW, Acetonitrils and Bromophenols measured in samples before and after treatment were below the Levels of Quantification.

Except for Chloroform, where some results for samples (0,02 – 0,05 µg/l) before and after treatment at or slightly above the LoQ (0,02 µg/l) were measured. These values indicate, that Chloroform background concentrations within the test water in the Bremerhaven harbour waters are to characterise around 0,02 – 0,05 µg/l. From this results can not be concluded, that the treatment process cause higher levels for Chloroform. For this reason values near to the LoQ will not be considered in further discussion. An exemption is the detection of one value for Chloroform concentration before the treatment (0,68 µg/l). As this is the only higher value clearly above LoQ and was measured in the sample before the treatment, it is considered as an outlier without further concern for the evaluation.

AOX could be measured in some samples at very low concentrations (0,02 mg/l) at the LoQ, in samples before and after treatment and here the same can be applied as for Chloroform.

Nitrite concentrations especially for brackish and salt water are above the LoQ and show a high variability in samples in both treatments, before and after the BWTS. Here are shown the lowest and highest Nitrite concentrations for freshwater, brackish and salt water:

Freshwater:	before treatment:	< 0,007 – 0,009 mg/l
	after treatment:	< 0,007 – 0,148 mg/l
Brackish water:	before treatment:	0,009 – 0,512 mg/l
	after treatment:	0,14 – 0,524 mg/l
Salt water:	before treatment:	0,023 – 0,512 mg/l
	after treatment:	0,116 – 0,53 mg/l

Regarding this variability and to obtain a significant conclusion, if the data from samples before treatment are different compared to data after treatment a statistic analysis have been performed. For the statistic evaluation the program SYSTAT 12 was used. Data of freshwater samples could not be tested, because the variability was to low, to apply test statistic for investigation of significance of the variability. Because the data of brackish and salt water samples were not normal distributed, the nonparametric Mann-Whitney U Test Statistic including the appropriate descriptive statistic was applied.

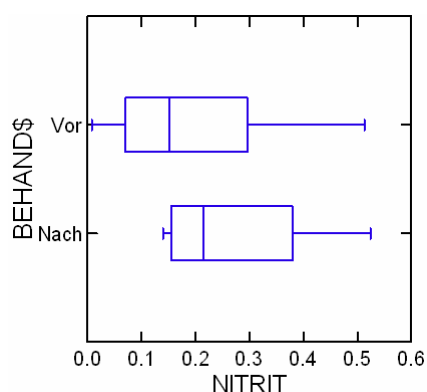


Figure 7: Box plot of descriptive statistic as part of the Mann-Whitney U Test Statistics of Nitrite concentrations before and after treatment of brackish water (Vor: before treatment, Nach: after treatment, middle line in the box: median, outer lines of the box plot: 25% and 75% quartile – representing 25% or 75% of the data within this range, n=14)

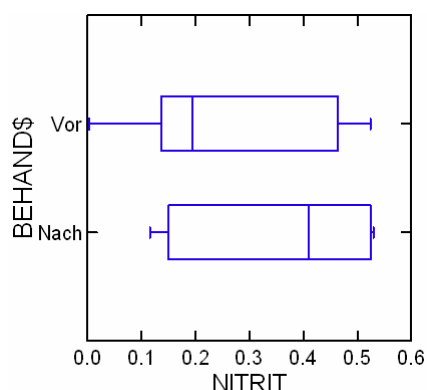


Figure 8: Box plot of descriptive statistic as part of the Mann-Whitney U Test Statistics of Nitrite concentrations before and after treatment of salt water (Vor: before treatment, Nach: after treatment, middle line in the box: median, outer lines of the box plot: 25% and 75% quartile – representing 25% or 75% of the data within this range, n=14)

In Figures 7 and 8 the box plots (descriptive statistic) of the estimation are shown. Number of data for brackish as well as for salt water for calculations before and after treatment were 14.

The result of the test statistic shows, the estimated P-values (0,27 for brackish water, 0,16 for salt water) were below the specified significance level of 95% ($\alpha = 0.05$). It can be concluded that Nitrite concentration from samples before and after the treatment belong to the same data population – means, they are significantly not different. From this it can be concluded, that the Nitrite concentrations measured in samples were not generated by the treatment process.

All Nitrite values before and after treatment are still within the German drinking water regulation, where 0,5 mg/l are the maximal allowed concentration at the user's tap. Hence no risk for human health and / or to the marine environment can be deduced on the basis of these data.

5.3 Risk characterization & analysis (G9: 5.3)

5.3.1 Reaction with Organic Matter (G9: 5.3.3)

Nitrite does not react with organic matter.

5.3.2 Characterization of Degradation Route & Rate (G9: 5.3.5)

Half-life of Nitrite has been estimated to be around 10 minutes, but turnover times strongly depend on the ambient conditions, especially the activity of nitrifying or denitrifying bacteria and the oxygenation of the water. As Nitrite is an essential part of the nitrogen cycle, their consumption is fast.

5.3.3 Prediction of Discharge & Environmental Concentrations (G9: 5.3.8)

On the basis of the chemical data determined in samples from the treated ballast water there is no indication of release of harmful substances, resulting in an increase of environmental concentrations.

5.3.4 Assessment of Potential for Bioaccumulation (G9: 5.3.7)

As there is no indication for the release of harmful substances, the actual potential for bioaccumulation is considered to be very low.

5.3.5 Effect Assessment on Aquatic organisms and sediment

Due to their extremely low life time, direct effects of photons and cavitation bubbles are not anticipated. In the effect assessment, only Other Chemicals as Nitrite are considered.

5.3.5.1 Risks to Aquatic Organisms

Acute and chronic toxicity data have been displayed in chapter 2.3.2.

The toxicity of Nitrite depends on a large number of factors, the most important being water chemistry and especially chloride concentration. With higher chloride concentration, toxicity decreases. Accordingly Schwörbel (1991) proposed the following environmental criteria.

0-3 mg Cl ⁻ /l	→ 33 µg/l NO ₂ ⁻
<3 – 7.5 mg Cl ⁻ /l	→ 164 µg/l NO ₂ ⁻
<7.5 - 15 mg Cl ⁻ /l	→ 296 µg/l NO ₂ ⁻
<15 – 30 mg Cl ⁻ /l	→ 394 µg/l NO ₂ ⁻
>30 mg Cl ⁻ /l	→ 493 µg/l NO ₂ ⁻

Bursch (2003) suggested a PNEC of 0,01 mg/l. These data correspond with the guidance values of the Fish Directive of the EU for Salmonid and for Cyprinid waters of $\leq 0,01$ mg/l NO_2^- and $\leq 0,03$ mg/l NO_2^- , respectively (EU Directive 2006/44/EC).

5.3.5.2 Risks to sediments and for bioaccumulation and secondary poisoning

Since Nitrite as an ion and therewith completely water soluble, for Nitrite does not exist a log K_{OW} value. Therefore neither sediment toxicity, nor bioconcentration or magnification effects, including secondary poisoning are considered to be of concern.

5.3.5.3 Risks to humans

No effects on humans are anticipated during the process (see Human health risk chapter). Exposure to treatment water could occur accidentally (e.g. people falling over board). As described above, concentrations of Other Chemicals in the treated ballast water are, however, considered to be too low to cause effects in aquatic organisms and will be unlikely to cause effects to humans that may become accidentally exposed to a mixture of treated ballast water and water.

Nitrite is strictly regulated in drinking water due to its known interference with the oxygen-carrying capacity of the blood which poses especially small children in danger.

Drinking water standards from the WHO, EPA, EU and Germany are depicted below (partly additional conditions with regard to Nitrate are included, which have been omitted here, as the focus is on Nitrite).

Regulatory body	Nitrite	
WHO	3 mg/l ⁴	Guideline value
EPA	1 mg/l ⁵	Maximum contaminant level
EU	0.5 mg/l ⁶	Quality standards have to be set by the member states but should not exceed the values of Appendix A of the drinking water directive
Germany	0.5 mg/l ⁷	The water that leaves the water treatment facility must not exceed Nitrite concentrations of 0.1 mg/l

Table 8: Drinking water standards from the WHO, EPA, EU and Germany for Nitrite

Derivation of guidelines for Nitrite contamination of drinking water are usually based on calculation of uptake per day per kg.

Extract from the WHO Drinking water guideline:

The guideline for Nitrite of 3 mg/l as Nitrite is based on human data showing that doses of Nitrite that cause methaemoglobinaemia in infants range from 0.4 to more than 200 mg/kg of body weight. By applying the lowest level of the range (0.4 mg/kg of body weight), a body weight of 5 kg for an infant and a drinking-water consumption of 0.75 litre, a guideline value of 3 mg/l (rounded figure) can be derived (WHO/SDE/WSH/07.01/16).

⁴ WHO/SDE/WSH/07.01/16

⁵ http://www.epa.gov/OGWDW/contaminants/dw_contamfs/nitrates.html

⁶ COUNCIL DIRECTIVE 98/83/EC

⁷ Trinkwasserverordnung 2001, chemische Parameter II

6 RISK ASSESSMENT

As per definition "risk" is determined by the equation

$$\text{Risk} = \text{Probability of occurrence} * \text{extent of loss / impact}$$

In the following the potential risks caused by the operation of the AquaTriComb™ ballast water treatment system technology as to the safety of the ship and to human health will be assessed.

This will be carried out by means of estimating the probability of occurrence of hazardous situations multiplied with the estimations on the extent of losses and / or scale of impact caused by such hazardous scenarios.

By definition of "prototyping" this risk assessment has to be a probabilistic approach rather than a deterministically based risk assessment. This, in turn, may result in the absence of data-base secured figures. In case of such lack of data-based figures a prescriptive approach will be applied.

6.1 Risk to Safety of Ship

6.1.1 Ship Integrity and the BWTS

The AquaTriComb™ plant will be installed *in line* after the ship's ballast water pump(s). Inlet and outlet piping are equipped with by-pass-valves and shut-off safety valves (Figure 1). The valves are fitted with flanges and will be equipped with electrically driven, and manual actuators.

If for certain reasons the BWTS operations have to be interrupted (service, maintenance, etc.) the plant will be by-passed by means of the by-pass-valves and closing of the safety valves. This design does not interfere with the ship's integrity.

The energy demand of the AquaTriComb™ 250 prototype is at approximately fifteen (15) kW. Although electrical load calculations on larger versions of the plant have not been finalized yet the probability that the energy demand would interfere with the on-board power supply, that is the auxiliary diesel-generator sets, is rather low.

With regard to the additional weight the prototype version is at approximately one point six (1.6) tons at 250 m³/h volume flow rate. A slightly flattened linear increase is expected for the larger versions, for example the 2000 m³/h version would be at approximately 10 to 12 tons. This weight equals half the gross weight of a loaded twenty-foot standard container (20' container maximal gross weight equals 24 tons). Therefore, also the additional weight of the BWTS would not impact the integrity of the ship.

6.1.2 Corrosion

The AquaTriComb™ technology is characterized by the absence of any Preparations or aggressive additives. Therefore no corrosion supporting, or corrosion stimulating effects are connected to the technology.

The effects of acoustic cavitation, which are generated by the ultrasonic oscillation, are strictly restricted to the interior of the MicroSintFilter (MSF) modules, respectively. Transfer of acoustic cavitation is system-dependent excluded, and piping or other components of the ship are not effected.

All the internal components of the AquaTriComb™ BWTS are designed and construed to match the effects of acoustic cavitation.

6.1.3 Fire and Explosion

The electrical and electronic parts of the AquaTriComb™ BWTS are intrinsically safe. There is no risk of fire or explosion associated with the system.

6.1.4 Noise and vibration

The noise level generated by the AquaTriComb™ BWTS is far below the permissible average noise level at the work place of 85 decibel (A), according to EC guidelines 2002/44/EG and 2003/10/EG (BGBI 2007).

Vibration level caused by the ultrasonic oscillation is rather low and noticeable only in direct contact with the MSF modules and the UV-reactor (hand touch).

In addition, the plant will be installed on vibration mounts for the protection of the plant itself and to reduce in-water noise emissions to a minimum.

6.1.5 Conclusion: Risks to Safety of Ship

The risks to the safety of the ship caused by the installation and operation of the BWTS AquaTriComb™, which is defined by the probability of the occurrence of a dangerous situation originated by the plant and the extent of impact, is not measurable by means of non existence.

This covers the ship's integrity, corrosion, fire and explosion as well as noise and vibrations. If the ship itself makes for a dangerous scenario like fire, explosion, structural damage or loss etc. the risks originated by the BWTS remain at zero as intrinsic safety is maintained and power shut-off is most probable.

6.2 Risks to human health

The AquaTriComb™ technology exclusively applies non-hazardous physical means of ballast water treatment which pose no risks to human health, that is

- Ultraviolet radiation (UV), and
- Ultrasonic oscillation (US).

The application of UV and US, however, generates Active Substances, explicitly photon and cavitation bubbles, which in turn results in OH radicals (Relevant Chemical) and by-products (Other Chemical).

The generation of OH radicals and by-products are confined to the feasible minimum by means of the application of exclusively UV-C radiation at 254 nm wave length. Also, by the application of US-oscillation at 20 kHz for a very limited time period of less than one (1) second only the size of the cavitation bubbles is as small as possible, and the effect of OH radical generating physical sonoluminescence is reduced to the most practicable minimum.

Therefore, OH is considered not resident in the treated ballast water and causes no harm to human health or to the environment.

In case OH radical related eco-toxicological by-products (Other Chemicals) are generated this will be on a level below the LoQ of the analytical methods. Thus by-products were not detectable in ballast water treated by AquaTriComb™ BWTS. In addition, occurrence of UV radiation and Ultrasound are limited to the hermetically enclosed MSF and UV-reactor, and risks to human health can be excluded.

6.2.1 Human Exposure Assessment

Because exclusively physical means of ballast water treatment are applied with the AquaTriComb™ technology the exposure assessment focuses on potential exposure as to

- UV-radiation
- Ultrasound oscillation
- and OH and by-products.

Potential exposure to Ultraviolet (UV) radiation: Inside the hermetically enclosed UV-reactor UV-C-radiation is generated by eighteen (18) high performance, low pressure mercury germicidal lamps with a filtered and selected wave length of approximately 253,7 nm.

The tube casing of the AquaTriComb™ UV-reactor is made of stainless steel (V4A) of 3 mm thickness. The top and bottom plating are made of 30 mm V4A and bolted (26 * M24) to the welded casing flanges. Top plating cable fairleads are welded and additionally covered by aluminium coverage. All welding and bolt connection are according to respective technical norms and standards and performed by accredited and certified workmanship. Therefore the probability of regular and/or accidental emission of UV-radiation equates zero.

Potential exposure to Ultrasound (US) oscillation: The ultrasonic tube oscillators (RS 20-48-9, compare data sheet) are located along the centre line inside the MicroSintFilter (MSF) modules and inside the UV-reactor. Oscillation is at twenty (20) kHz with a maximal capacity of 1.000 W, thus permanently preventing particle accumulation in the MSF modules, and des-agglomeration of organic particles, detritus, colony forming algae and other agglomerates (bio film) at the surface of the mercury germicidal lamps.

The MSF modules are identical in design and construction as the UV-reactor, which results in no release of ultrasound and no impact to human health.

Potential exposure to OH and by-products: As stated above, the concentration of OH and by-products would be on such a low level that risks to human health can be excluded. Therefore, risks to human health by means of exposure to Relevant or Other Chemicals can be excluded.

In applying the Margin of Safety (MOS) or Margin of Exposure (MOE) approach, the equation would consequently result in No Observed Adverse Effect Level (NOAEL).

6.2.1.1 Hazard identification

In **regular operation mode** of the AquaTriComb™ BWTS no hazards to human health can be identified:

- No persons are exposed to UV radiation
- Low level casing vibration caused by US oscillation inside MSF modules does not pose any hazard
- No contact with non-hazardous concentration of potential Relevant or Other Chemicals.

In **service & maintenance (S&M) mode** hazards are limited to illegal and / or intentional risk exposure:

- Non switch-off of energy supply before S&M works with the risk to exposure to UV-C radiation
- Operational procedures, alert signing and emergency shut-off device will prevent such scenario (to be integrated into shipboard SMS-manual⁸).

In **incidental / accidental mode** such as shipboard fire, explosion, black-out, structural loss etc. most probably energy supply to BWTS will be cut-off anyhow and / or BWTS will have malfunction.

6.2.1.2 Exposure assessment

Regular operation & maintenance procedures (O&M) on board ship include inspection of sea chest and sea water / ballast water piping and pumps, and related services. For such action the BWTS will be shut-down, thus no exposure to UV-radiation or chemicals will appear. This also counts for dry docking and / or annual classification services in dock / alongside the pier.

Due to high quality plant components and materials service and maintenance intervals of the BWTS are extremely low. The exchange of the ultrasonic tube oscillators are calculated after a minimum of approximately 16,000 operational hours, the exchange of the low pressure mercury germicidal lamps are calculated after circa 12,000 operational hours.

As no Preparations are utilized or generated by the AquaTriCombTM BWTS normal and good workmanship practise is to be applied by the personnel involved (gloves and mask).

No additional or special pre-caution measures are recommended or necessary.

6.2.2 Conclusion: Potential Human Health Risks

Normal operation and maintenance (O&M) procedures of the AquaTriCombTM BWTP do not pose any risks to human health, nor acute, neither mid / long-term exposure situations are realistically probable. This statement covers all population groups including crew, service technicians, passengers and personnel, public and port persons, or consumers of seafood and persons at the coastline.

The probability of incidental and/or accidental health risks caused by the AquaTriCombTM BWTP are limited to catastrophic or worst-case scenarios, although almost implausible.

The absence of any Preparations reduces such risks to shipboard fire, explosion, structural damage/loss and similar casualties. In occurrence of such catastrophic events it is assumed that the power supply to the BWTP is cut-off anyway, resulting in non-performance of UV-radiation and / or US-oscillation, and associated processes.

From the Risk Assessment carried out are no identifiable risks associated to the ship, it's personnel or other persons and / or parties concerned, which are originated by the installation and operation of the AquaTriCombTM ballast water treatment system.

This is mainly due to the fact, that the BWTP does not introduce any Preparations, Active Substances or Relevant Chemicals but the technology is a purely physical treatment technology. Further, the design and construction do not interfere with the vessel's integrity, and high-end components and materials guarantee reliable and sound performance.

⁸ SMS means Safety Management System according to the ISM-Code (ISM 2002)

6.3 Risks to the aquatic environment

6.3.1 Magnitude of Hazard from the Ballast water treatment process

In Table 9 is exemplary shown the PNEC (Predicted No Effect Concentrations) for Nitrite values in water.

Substance	Substance class	PNEC	Medium	Reference
Nitrite	Inorganic nutrient	10 µg/l	Water	

Table 9: Predicted No Effect Concentrations (PNEC) for Nitrite (Bursch 2003).

6.3.2 Probability of exposure

Exposure to Other Chemicals could occur through the emitted treated ballast water. According to the chemical analyses, none of the Other Chemicals, discussed in this report, are produced significantly above LoQ, as can be concluded from the chemical data directly (results are shown in Tables A1 – A3 Annex, see also Table 8 LoQ for all substances) expect the Nitrite values, which shown by statistic evaluation are not caused by the treatment process.

6.3.3 Assessment of Environmental Risk

On the basis of the results of analysis of several theoretical possible by-products at this stage of the assessment it can be concluded that there is no indication for an environmental risk from this treatment process.

6.3.4 Conclusion on Risk to Human health

Exposure of humans to the active substances is not possible. Exposure to potentially Other Substances in the treated ballast water would theoretically be possible but with low probability. Effects are highly unlikely due to the low aquatic toxicity.

Toxic effects through volatile substances such as chloroform would theoretically be possible. No increased concentration of e.g. chloroform, however, could be measured. Therewith there is no indication of risk to human health from any substances produced in the process at this stage.

7 ASSESSMENT REPORT (G9: 4.3)

7.1 Overview of Data and Endpoints

During the AquaTriCombTM-process aquatic organisms will be affected by photons and cavitation bubbles. Both are short lived and their presence is restricted to the duration of the UV and US application, locally to the treatment reactor.

Exposure to the aquatic environment from substances termed Other Chemicals, which can be produced indirectly through photons or cavitation bubbles, could occur after discharge of the treated ballast water.

As shown by chemical analysis of water samples before and after ballast water treatment, concentrations of all observed substances were below the LoQ. Therefore no indication of release of harmful substances, resulting in an increase of environmental concentrations could be observed. Except for Nitrite, which data above the LoQ showed a high variability of concentrations. Statistical analysis indicate that data before and after treatment are not significantly different. Therefore the treatment process is not responsible for the observed Nitrite values.

As there is no indication for the release of harmful substances, the actual potential for bioaccumulation is considered to be very low. Neither sediment toxicity, nor bioconcentration or magnification effects, including secondary poisoning are considered to be of concern.

From the Risk Assessment carried out are no identifiable risks associated to the ship, its personnel or other persons and / or parties concerned, which are originated by the installation and operation of the AquaTriComb™ ballast water treatment system.

On the basis of the results of analysis of several theoretical possible by-products and the risk assessment it can be concluded that there is no indication for a risk to the aquatic environment and/or humans based on the treatment process of the AquaTriComb™ BWTS.

7.2 Test Report Data Quality

References used for this approval comprise Risk Assessment studies from Euro Chlor, the European Commission, WHO, and US EPA, which critically evaluated their data basis with regard to accreditation of laboratories, standardization of test systems and documentation of results.

Further more, peer reviewed articles were used to gain detailed information. The PAN Pesticide data base proved to be very helpful. All of its information is backed up by rigorous scientific studies and most of the data are taken from official sources of weight-of-the-evidence-type evaluations when they are available. For more information of data accuracy of the data base: <http://www.pesticideinfo.org/Docs/data.html#AccuracyofData>

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